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Diffusion of Titanium in Zirconium-Hydrogen and Zirconium-Deuterium Alloys

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Abstract – The electron probe microanalysis technique has been used to measure the interdiffusion coefficients in the diffusion couples titanium-zirconium and titanium-zirconium alloys with hydrogen and deuterium in the range of existence of the bcc β-phase. Hydrogen and deuterium dissolved in zirconium have been shown to increase the activation energy for the diffusion of substitutional atoms. On the basis of the interdiffusion data obtained, a thermodynamic analysis of the H- and D-doped Ti–Zr alloys has been carried out and the melting temperatures of zirconium hydride and deuteride have been determined.

INTRODUCTION

The saturation of a titanium alloy with hydrogen is known to considerably increase its deformability under certain conditions [1]. The mechanical properties of metals depend on a number of factors. One of the possible reasons which may account for the above increase in the deformability is the growing diffusion mobility of metal atoms in the matrix upon its saturation with interstitial hydrogen atoms. There exists no single answer to the question of how hydrogen affects the self-diffusion and heterodiffusion of a substitutional impurity in a metal matrix. This problem is not of purely applied value and enters as a constituent part into a large and still insufficiently studied problem concerning the effects of the interstitial impurities (which are situated in the interstices and capable of travelling in the lattice with no vacancies involved) on the diffusion of the matrix atoms (occupying the lattice sites and moving only by exchanging places with the vacancies).

We have studied the heterodiffusion of titanium in zirconium saturated with hydrogen or deuterium. Titanium and zirconium are known to have a phase diagram with complete mutual solubility in the solid state, both above and below the polymorphic transformation from the hcp α-phase to the bcc β-phase [2]. To simplify the problem, the diffusion has been studied at temperatures above this transition.

The solubility of both H and D in the β-phase of titanium and zirconium is sufficiently large, approaching 50 at % [2]. In the above temperature range, the partial pressure of hydrogen over TiH_x alloys is several times that over the ZrH_x alloys with the same hydrogen concentration (for example, at $T \simeq 930$°C these are 10^5 and 1.3×10^4 Pa for $TiH_{0.5}$ and $ZrH_{0.5}$, respectively [3]). The diffusion coefficients of H and D in the metals being greater by several orders of magnitude as compared to those of the substitutional atoms, the chemical potential of the interstitials during the diffusion anneal can be assumed to have the same value everywhere in the diffusion couple. This implies that in a diffusion couple composed of titanium and zirconium, the hydrogen isotope will be contained mainly in Zr, while its concentration in the diffusion zone will decrease gradually with growing Ti concentration down to a nearly zero level in the pure titanium region. If hydrogen is introduced into titanium at the beginning of anneal, it will predominantly migrate to zirconium through the gas phase before any noticeable interdiffusion of the metallic components will take place. Therefore, our problem formulation implies that the dependence of the interdiffusion of metals on the interstitial impurity concentration can be studied only in the zirconium-rich domain. Such an approach seems to be well supported as far as the first estimates are concerned.

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EXPERIMENTAL

The initial materials were iodide titanium and zirconium purified by electron beam melting in a vacuum. After this, the carbon content in titanium was 0.01 at % and that of oxygen was 0.02 at %. Two zirconium-hydrogen and two zirconium-deuterium alloys were prepared:

$ZrH_{0.11}$(Zr–9.6 at % H) and $ZrH_{0.29}$(Zr–22.6 at % H);

$ZrD_{0.13}$(Zr–11.5 at % D) and $ZrD_{0.37}$(Zr–27.0 at % D).

For the alloys preparation, the proper amounts of zirconium cut from the same ingot were annealed at 800 °C for 20 min in a vacuum of 10^{-7} Pa. Then a definite amount of hydrogen isotope obtained by thermal decomposition of TiH_2 or TiD_2 was admitted into the reactor containing the metal. The major part of hydrogen (deuterium) was absorbed in the course of the gas admission, and the remainder, during a slow (about 5 h) cooling of the furnace.

The isotope concentration was determined within a 1 at % accuracy by weighing the samples before and after the saturation. The spark-cut samples for diffusion anneals had the form of "quarters" of a cylinder with a diameter of 19 mm and a height of 3 mm (zirconium) and 2 mm (titanium). The contact surfaces of titanium and zirconium-alloy samples were mechanically ground and polished. On the surface of zirconium

alloys, a 5 - 10 μm thick titanium layer was then deposited by ion-plasma sputtering. Prior to the titanium application, the sample surface was cleaned by glow discharge in argon for 5 min in situ in the deposition chamber. Thus, the subsequent diffusion anneal involved a contact not between titanium and zirconium, but rather between bulk titanium and the titanium layer deposited on the zirconium surface. Therefore, the surface of primary Ti–Zr contact was formed not under relatively dirty conditions in the ampoule for diffusions anneals, but rather in a vacuum of 10^{-7} Pa immediately after glow-discharge cleaning the sample surface.

The diffusion couples Ti–$ZrH(D)_x$ were tied together with a molybdenum wire and sealed in evacuated (to about 10^{-5} Pa) quartz ampoules. The alloys with different concentrations of hydrogen and deuterium were placed in different ampoules. The internal volume of the ampoules was 3 - 5 cm^3. Each ampoule contained also about 1 g titanium cuttings to absorb the residual gases. For the reasons mentioned above, the effect of this on the hydrogen redistribution was assumed to be negligible. Four diffusion anneals were carried out at temperatures of 943, 983, 1023, and 1063°C; their durations were 48, 63, 44.5, and 48 h, respectively. The temperature during the anneal was maintained within ±2°C.

After annealing, the samples were encapsulated with Wood's alloy in cylindrical mounts. Then a 1 - 1.5-mm thick layer was mechanically removed perpendicularly to the diffusion interface. The section surface was ground on emery paper and polished on a lap with Cr_2O_3 powder.

The zirconium concentration profiles in the sections obtained was studied by the electron probe microanalysis technique on a JXA-5 spectrometer. All corrections necessary for quantitative analysis were introduced according to Ref. [4]. No Kirkendall voids were detected in the diffusion zone in any of the samples studied, in accordance with the other Ti and Zr interdiffusion studies [5, 6]. For this reason, no special markers were introduced in the initial Ti–Zr contact interface.

An example of the initial titanium depth-concentration profile in the diffusion zone is presented in Fig. 1. This distribution was obtained by annealing the Ti–Zr diffusion couple at 983°C. The concentration dependence of the interdiffusion coefficient was obtained using the simplest discrete version of the Matano method [7]. The function $c(x)$ was tabulated with a concentration step of 2%, and the corresponding coordinates were determined as the midpoints of the intervals of intersection of the coordinate distribution with the axis $c = c_i$. The errors of the diffusion coefficient determination by this method, although relatively high for each particular measurement, are averaged upon determining the whole curve. The effects studied fell far outside the uncertainty of measurements, so that the simple calculation procedure described above was quite sufficient to solve the problem formulated.

EXPERIMENTAL RESULTS

The interdiffusion coefficient $\tilde{D}$ in all the alloys studied depends noticeably on the metal component concentration C. All the $\tilde{D}$ versus C plots exhibit a maximum in the range of 30 - 60 at % Ti. An example of such a plot obtained for the Ti–Zr couple annealed at 1063°C is given in Fig. 2. The maximum of the $\tilde{D}(C)$ function reflects a minimum existing in the solidus curve for the Ti–Zr system [2]. A similar correlation between the shape of the concentration dependence of the interdiffusion coefficient and that of the solidus curve was also observed in other systems such as Co–Mn [8], Co–Pd [9], and Co–Pt [10].

Figs. 3a - 3e show the temperature dependence of the interdiffusion coefficient $\tilde{D}$ in all the systems studied. Each family represents the $\tilde{D}$ values for the titanium concentrations of 30 and 20 at % and the value obtained by interpolation to 0 at % Ti. The magnitude

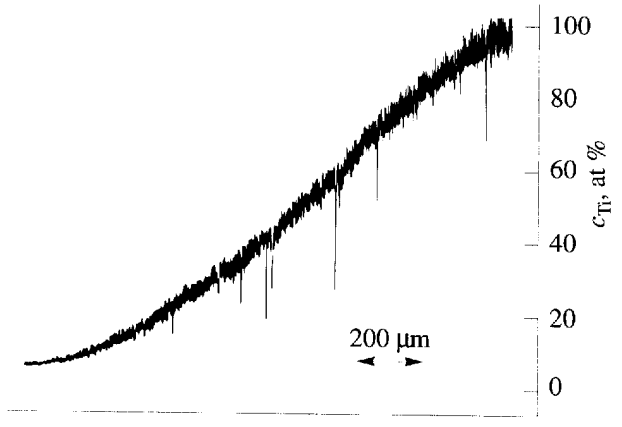

Fig. 1. *Titanium concentration profile in the diffusion zone of the Ti–Zr couple annealed at 983°C.*

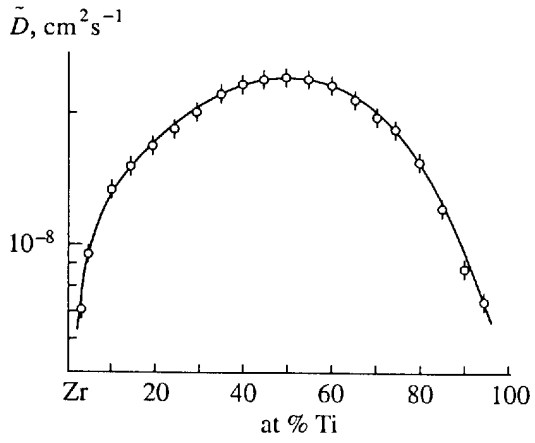

Fig. 2. *Interdiffusion coefficients versus composition in the system Ti–Zr annealed at 1063°C.*

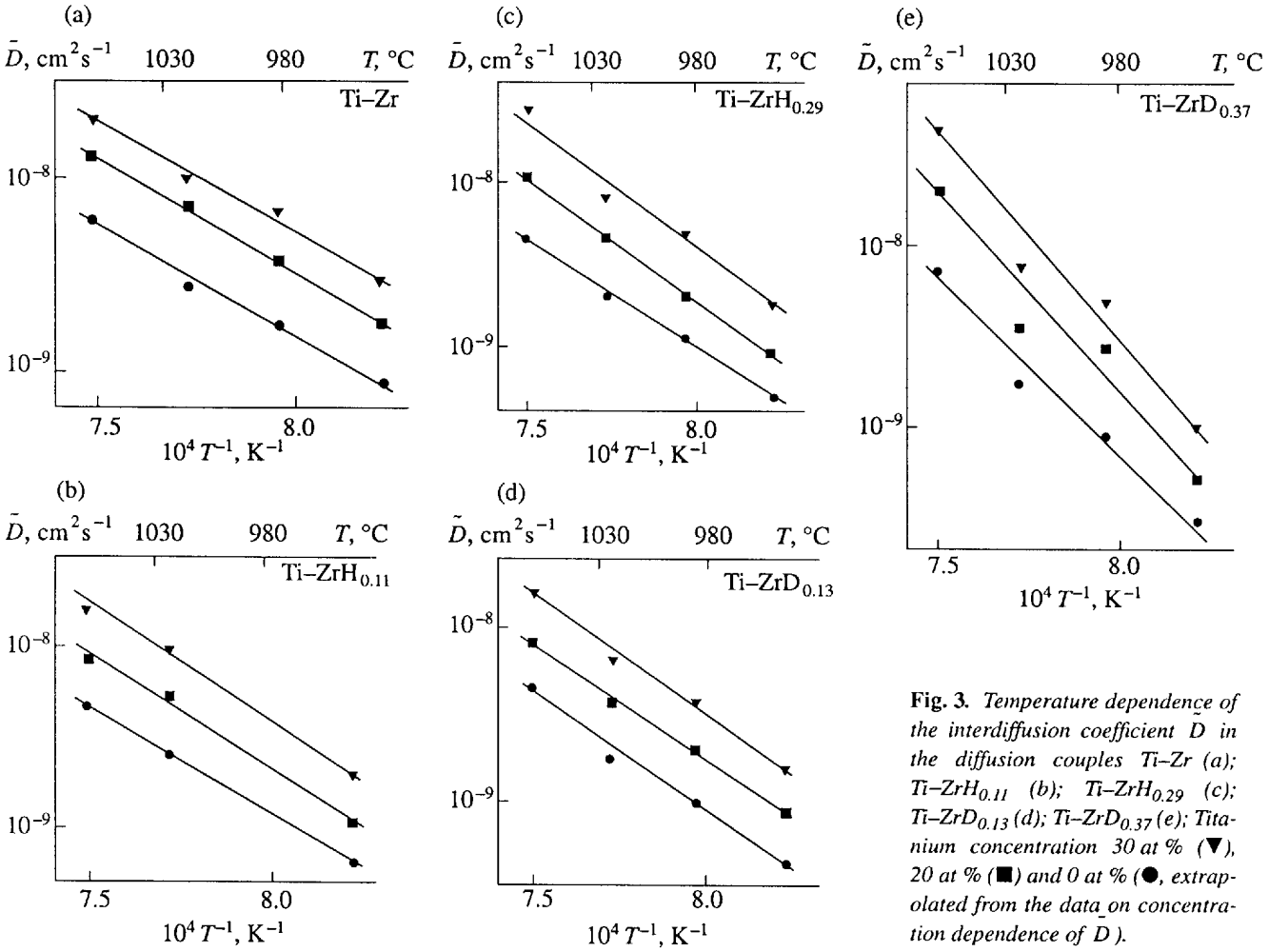

Fig. 3. *Temperature dependence of the interdiffusion coefficient $\tilde{D}$ in the diffusion couples Ti–Zr (a); Ti–ZrH$_{0.11}$ (b); Ti–ZrH$_{0.29}$ (c); Ti–ZrD$_{0.13}$ (d); Ti–ZrD$_{0.37}$ (e); Titanium concentration 30 at % (▼), 20 at % (■) and 0 at % (●, extrapolated from the data on concentration dependence of $\tilde{D}$).*

of $\tilde{D}$ always grows with the titanium concentration. We shall not discuss the temperature dependence of the interdiffusion coefficient at still higher titanium concentrations because the content of H or D drops (as has been pointed out above) upon going from zirconium to titanium in the diffusion zone. The activation energies E_{act} and preexponential factors $\tilde{D}_0$ are given in Table 1. Both the activation energy for interdiffusion and the preexponential factor are found to grow noticeably with the concentration of hydrogen or deuterium (Fig. 4), the latter producing a greater increase in the E_{act} as compared to hydrogen. No such unambiguous conclusion can be made, however, with respect to the interdiffusion coefficient, since at various temperatures, H and D concentrations, and titanium contents, the coefficient $\tilde{D}$ can be either higher or lower than that in the Ti–Zr system free of hydrogen or deuterium (Fig. 5). The data of Fig. 5 suggests that at $T \lesssim 1000$°C, where the hydrogen-induced increase of the deformability of titanium alloys is usually observed, the hydrogen doping of the

Table 1. Activation energies E_{act} and preexponential factors $\tilde{D}_0$ for the interdiffusion coefficients in Ti–ZrH(D)$_x$ alloys with various titanium concentrations (at %)

Alloy	E_{act}, kcal mol^{-1} (±2 kcal mol^{-1})			$\tilde{D}_0$, cm^{2}s^{-1}		
	30	20	0	30	20	0% Ti
Ti–Zr	54	55	52	20	10	2
Ti–ZrH$_{0.11}$	60	57	52	100	20	1
Ti–ZrH$_{0.29}$	68	67	57	3×10^3	700	10
Ti–ZrD$_{0.13}$	63	60	61	300	40	40
Ti–ZrD$_{0.37}$	103	100	88	3×10^9	4×10^8	2×10^6

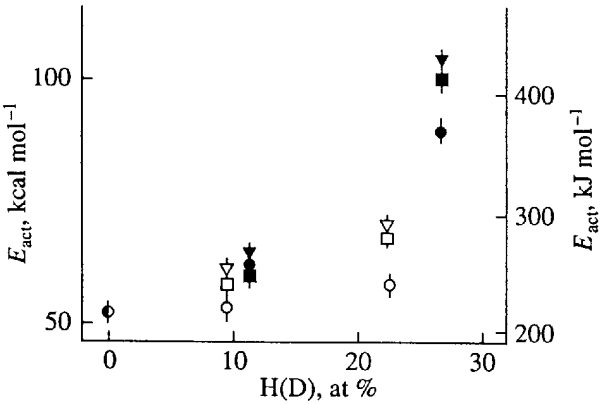

Fig. 4. *Interdiffusion activation energy versus the concentration of hydrogen and deuterium. The data refer to various Ti concentrations. Notation as in Fig. 3. Open symbols represent alloys with hydrogen, and solid symbols, alloys with deuterium. The Ti–Zr system without H and D is represented by a half-filled symbol.*

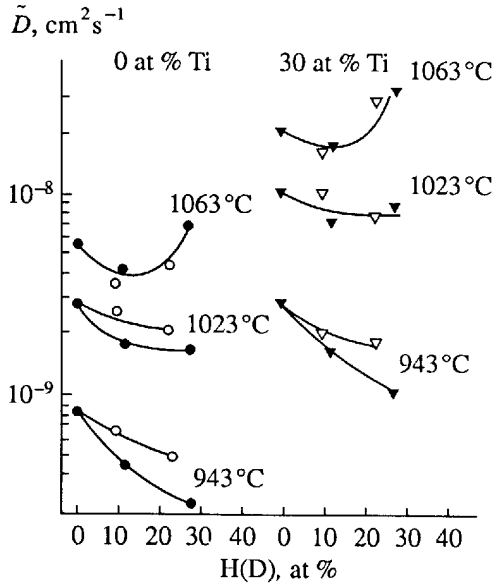

Fig. 5. *Interdiffusion coefficients versus hydrogen and deuterium concentrations at various temperatures for the systems with 30 at % Ti and 0 at % Ti. Open symbols represent alloys with hydrogen, and solid symbols, alloys with deuterium and a Ti–Zr couple without additions.*

particular Ti–Zr system studied produces a decrease in the interdiffusion coefficient of the metal component.

DISCUSSION OF RESULTS

(1) Let us compare our results on the interdiffusion of Ti and Zr in the absence of hydrogen and deuterium with the literature data [5, 6]:

(i) the values of the diffusion coefficients at comparable temperatures differ by a factor of 3 - 5;

(ii) the $\tilde{D}(C)$ plots presented in Ref. [5] exhibited small maxima at about 50 at % Ti; in Ref. [6] the diffusivity showed virtually no concentration dependence. Unlike this, we have observed strongly pronounced maxima at 30 - 60 at % Ti;

(iii) in the temperature range from 900 to 1100°C, the activation energy of interdiffusion was reported in Ref. [5] to be 31 - 26 kcal mol^{-1} (for various titanium concentrations), and in Ref. [6], 33 - 39 kcal mol^{-1}. Our results vary within 55 - 60 kcal mol^{-1}. The preexponential factors in the three cases were 10^{-4} to 10^{-5} [5], 10^{-3} to 10^{-2} [6], and 1 to 10 cm^2 s^{-1} (our data).

In our opinion, the observed scattering of the data is accounted for by strong interaction of Ti and Zr with the interstitial impurities, so that even small variations in the sample preparation procedures may considerably affect the kinetic behavior. We have intentionally doped the samples with various amounts of hydrogen and deuterium, the other materials and experimental conditions being identical. This allows us to make definite conclusions on the effects of interstitial impurities, hydrogen and deuterium, on the diffusion in the system studied.

(2) In most metals, the activation energy for the diffusion of substitutional atoms obeys simple semiempirical correlations. These relate E_{act} to the melting temperature or solidus temperature T_s. For example, according to Ref. [10] this last correlation can be expressed as $E_{act} \cong 18RT_s$. The parameters of diffusion activation in some anomalous bcc metals, however, fail to satisfy this relation. Titanium and zirconium are the very metals where the diffusion anomalies are most sharply pronounced. According to the literature data available, these metals exhibit strong deviations from the Arrhenius law in the β-phase at temperatures close to the $\beta \rightarrow \alpha$ transition temperature [5, 11, 12]. The diffusion activation energy near the $\beta \rightarrow \alpha$ transition proves to be considerably lower than that observed at elevated temperatures. There exist two principal explanations of this anomaly. These are, however, far from excluding each other and can be formulated as follows:

(i) near the $\beta \rightarrow \alpha$ transition temperature, the diffusion involves, besides the usual, some other mechanism, e.g., by divacancies;

(ii) the increased diffusivity is due to the presence of excess vacancies bound to oxygen.

There also have been some attempts to describe the anomalous diffusion in terms of heterophase fluctuations [13].

According to semiempirical estimates, the activation energy for interdiffusion of Ti and Zr is $E_{act} = 18RT_s = 74$ kcal mol^{-1}. Our data suggests that upon doping zirconium with hydrogen or deuterium, the interdiffusion activation energy increases and may even exceed the above estimate. It is not excluded that hydrogen and deuterium "compensate" the anomalous diffusion properties of zirconium. Now we shall try to analyze the possible reasons underlying the effects of H and D on the self-diffusion of substitutional atoms.

The self- and heterodiffusion in substitutional alloys is known to be strongly affected by the interstitial carbon and oxygen atoms [14]. The theory of this phenom-

enon proposed in Ref. [15] was based on a simple microscopic diffusion model. According to this, for all permissible values of the interaction energy of interstitials with the atoms of metal matrix, the self-diffusion activation energy of the last one drops, while the self-diffusion coefficient increases. The model of Ref. [15] shows that the reverse effect is, generally speaking, also possible, but the resulting activation energy increment is very small and hardly experimentally detectable. Therefore, in order to explain the observed growth of the E_{act} and D_0 values with the increasing concentration of hydrogen or deuterium, it is necessary to resort to some additional factors. Such a physical reason producing a growth in the activation energy and preexponential factor can be a strong interaction of interstitials with vacancies not taken into account in Ref. [15]. We shall not, however, dwell here on constructing a detailed microscopic model, but restrict the consideration to simple semiempirical correlations.

From points (1) and (2), it follows that the activation energy of diffusion in an alloy increases with growing melting temperature. It is known that hydrides and, hence, deuterides, of titanium and zirconium melt at a higher temperature than do the metals themselves [3]. This implies that an addition of hydrogen or deuterium must produce an increase in the solidus temperature T_s and, hence, in the activation energy of diffusion in the alloy, just as it has been observed in our experiments. Unfortunately the melting temperatures of hydrides and deuterides of Ti and Zr are unknown. We can, however, estimate these from our diffusion data and compare the result with the melting temperatures of the other interstitial phases of zirconium. To this end, we shall use the correlation between E_{act} and T_s in the form $E \cong 18RT_s$ [14]. Let the Zr hydride contain 50 at % hydrogen. By extrapolating the E_{act} data of Fig. 4 to 50 at % H or D, we obtain:

$$E_{act} \simeq 65 \text{ kcal mol}^{-1} \text{ (for 50 at \% H)};$$

$$E_{act} \simeq 115 \text{ kcal mol}^{-1} \text{ (for 50 at \% D)},$$

from which the melting temperatures of Zr hydride and deuteride are 2200 and 4100°C, respectively. These values are close to the estimate of Ref. [16]. For comparison, it should be also noted that the melting temperatures of carbide ZrC, nitride ZrN, and boride ZrB_2 are 3175, 2980, and 3040°C, respectively [2].

(3) The diffusion data obtained in our work allow one to estimate the effects of hydrogen on the thermodynamic properties of the Ti–Zr solution. It is known that for a large number of solid solutions with unlimited solubility, the diffusion coefficient D can be expressed as [17]

$$\tilde{D} = (D_{AB}g_{AB}) / \exp\left[\frac{16\Delta T_s}{RT}\right], \quad (1)$$

where g_{AB} is the thermodynamic factor;

$$D_{AB} = N_A D_A^0 + N_B D_B^0$$

is the diffusivity determined by the straight line passing through the points corresponding to the diffusion coefficients, D_A^0 and D_B^0, of the pure components (N_A and N_B are the molar concentrations);

$$\Delta T_s = T_s^{AB} - N_A T_m^A - N_B T_m^B$$

is the difference between the solidus temperature and the temperature calculated for the straight line connecting the melting points, T_m^A and T_m^B, of the pure components.

The results of calculation of the g_{AB} values for the diffusion anneal at 1023°C are presented in Table 2. The condition $g_{AB} > 1$ implies the tendency to order the Ti–Zr solid solution. It also is seen that the g_{AB} values decrease somewhat with growing hydrogen content in the alloy. This can be due to the fact that hydrogen reduces the tendency of the Ti–Zr solution to order [18]. Within the accuracy of our experiments, the g_{AB} value is virtually independent of the deuterium content. However, the calculations by Eq. (1) imply the use of the phase diagram of Ti–Zr system without hydrogen or deuterium. As has been noted above, the presence of deuterium strongly affects the solidus temperature.

CONCLUSIONS

(1) Doping zirconium with hydrogen and deuterium produces a growth in both the activation energy and preexponential factor of the coefficient of chemical diffusion of titanium.

(2) Hydrogen and deuterium additions make the diffusion properties of zirconium matrix close to those of usual (rather than anomalous) metals.

(3) Deuterium increases the activation energy of diffusion of the matrix atoms to a greater extent than does hydrogen.

(4) The melting temperatures of zirconium hydride and deuteride estimated from semiempirical correlations are 2200 and 4100°C, respectively.

Table 2. Concentrational dependence of the thermodynamic factor g for interdiffusion at 1023°C

C, at %	Ti–Zr	Ti–$ZrH_{0.11}$	Ti–$ZrH_{0.29}$	Ti–$ZrD_{0.13}$	Ti–$ZrD_{0.37}$
10	1.8 ± 0.3	1.6 ± 0.1	1.4 ± 0.1	1.7 ± 0.1	1.6 ± 0.1
20	2.2 ± 0.3	2.1 ± 0.1	1.8 ± 0.1	2.0 ± 0.1	1.9 ± 0.1
30	2.0 ± 0.3	2.1 ± 0.1	1.8 ± 0.1	2.0 ± 0.1	2.0 ± 0.1
40	1.7 ± 0.3	1.9 ± 0.1	1.7 ± 0.1	1.9 ± 0.1	1.9 ± 0.1
50	1.5 ± 0.3	1.7 ± 0.1	1.5 ± 0.1	1.6 ± 0.1	1.7 ± 0.1

(5) Hydrogen and deuterium additions reduce the tendency to order in a solid solution of β-Ti–β-Zr.

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