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Reaction diffusion in the vanadium–zirconium system

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Reaction diffusion in the vanadium–zirconium system has been studied in the temperature range 1273 to 1473 K by use of two types of semi-infinite couples, (pure V)–(pure Zr) and (pure V)–(Zr–13.5 at % V alloy) and a sandwich type couple, (pure V)–(pure Zr foil of 50 to ~200 μm)–(pure V). In all three types of couples diffused above 1373 K parabolic growth of the V_2Zr phase layer has been observed after respective incubation times. At 1473 K, the incubation time in the (pure V)–(pure Zr) couple is 24 h, however, it is 1 h in the (pure V)–(pure Zr foil of 50 μm)–(pure V) couple and nearly zero in the (pure V)–(Zr–13.5 at % V alloy) couple. This suggests that for nucleation of the V_2Zr phase during the reaction diffusion, the concentration at the interface of the phase boundary between the β-phase (Zr-rich solid solution) and the γ-phase (V-rich solid solution) is required to reach the nearly equilibrium one. It has been found that at the lower diffusion temperature the uphill diffusion of vanadium from the β–phase contributes in part to growth of the V_2Zr layer. In addition to the V_2Zr phase, another phase, VZr, unexpected from the equilibrium phase diagram of the V–Zr system has been formed in the (pure V)–(pure Zr) couple diffused at 1473 K for more than 230 h.

1. Introduction

To investigate the mechanism of reaction diffusion and kinetics of layer growth of intermetallic compounds in the diffusion couple is of both academic and technological interests. Industrially important processes involving reaction diffusion include aluminide coating of nickel-base alloys, fabrication of superconducting compounds and numerous applications in semiconductor device construction. Fundamental interests in reaction diffusion involving multilayer growth are whether diffusion limited growth occurs, whether all the phases predicted by the phase diagram appear and whether the interface compositions approach those predicted by the equilibrium phase diagram. Previous investigations have shown that the equilibrium phases existing in the phase diagram do not always appear in interdiffusion couples and that, as in precipitation in alloys, the appearance of metastable phases is possible. From these points of view, it is worthwhile to study the reaction diffusion between two metals or alloys which have very different diffusional properties from each other, and especially form a simple binary system with only one intermetallic phase. However, only a few studies in this aspect have been made [1, 2].

Among the bcc refractory metals vanadium belongs to the low self-diffusivity metals. On the other hand, bcc zirconium is one of the anomalous metals which has a very high self-diffusivity and shows a considerable deviation from the linear Arrhenius relationship in the temperature dependence of the self-diffusivity. For example, the ratio of the self-diffusion coefficient in zirconium [3] to that in vanadium [4] is 10^5 and 3×10^3 at 1273 and 1473 K, respectively. Furthermore, the ratio of the impurity diffusion coefficient of vanadium in zirconium [5] to that of zirconium in vandium [6] is 2.6×10^4 and 10^3 at 1273 and 1473 K, respectively. Thus the diffusional property of vanadium is very much different from that of bcc zirconium. Although the solvus in both

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phases has not been determined precisely, the reported maximum solid solubility of vanadium in the β-phase (Zr-rich solid solution) is around 16.5 at% at 1503 K and that of zirconium in the γ-phase (V-rich solid solution) is around 7 at% at 1573 K [7]. The V_2Zr phase, which is only one intermetallic compound in the proposed equilibrium phase diagram, is an excellent superconductor of the C15 structure with high critical current density and high upper critical field [8]. However, no systematic study of the formation of the V_2Zr phase by the reaction diffusion in the binary V–Zr system has been made, although fabrication of the C15 superconducting compound by the reaction diffusion in the ternary V–Zr–Hf system has been studied by Inoue and Tachikawa [9, 10].

In the present work, experiments on the reaction diffusion in the V–Zr system have been carried out in the temperature range 1273 to 1473 K to examine the formation and growth kinetics of the intermetallic phase.

2. Experimental procedure

Pure vanadium and zirconium rods were made by electron-beam melting vanadium flakes of 99.7% purity and zirconium sponges of 99.6% purity, respectively. The rods were machined to make block specimens of about 5 mm × 8 mm in section and 2 mm thick. Both faces of the specimens were ground on waterproof abrasive papers and polished on a buff with fine alumina paste (particle size; 0.3 μm). Finally, vanadium specimens were electropolished in a dilute HCl solution, and zirconium specimens were polished chemically in a solution containing HF, HNO_3 and H_2O with a volume ratio of 5, 45 and 50, respectively. A Zr–13.5 at%V alloy ingot was made by argon arc-melting the pure metals and machined to make specimens of the same size as the pure metals. All the grain sizes of the specimens of pure metals and the alloy were about 2 to 3 mm. Pure zirconium foils of 50 to 200 μm were made by rolling and annealing the zirconium rod. The block of the alloy and the pure zirconium foil were polished in the same way as the pure zirconium specimen. Two types of semi-infinite couples, (pure V)–(pure Zr) and (pure V)–(Zr–13.5 at%V alloy), and a sandwich type couple made by inserting a thin foil between two bulk metals, that is, (pure V)–(pure Zr foil of 50 to ~200 μm)–(pure V) were made. The couple was put in a stainless steel holder with two screws, pressed by the screws and diffusion-welded by heating in vacuum of 1.3 mPa at 1243 K for 1 h. The couple was removed from the holder and sealed in a quartz tube with argon gas of 99.9995% purity. Diffusion anneal was carried out at a temperature in the range between 1273 and 1473 K for 2 to 706 h in an electric resistance furnace controlled within ± 2 K.

After diffusion, the couples were cut parallel to the diffusion direction and the sections were polished in the same way as described above. An electron probe microanalyser (Shimadzu ARL-II EPMA) was used to determine the concentration–penetration profile in the diffusion zone of the couple. The operating conditions of EPMA were as follows: accelerating voltage, 20 kV; take-off angle of $VK\alpha$ and $ZrL\alpha$ X-rays analysed, 0.916 rad; specimen current, 10 nA; line scanning speeds, 5, 10, 20 or 100 $\mu m\,min^{-1}$. After anodic etching the diffusion zone in a solution of Na_2CO_3 (0.4 g), C_2H_5OH (50 ml), NH_4OH (10 ml) and H_2O (30 ml) with a stainless steel cathode at 100 V, the layer thickness of the intermetallic compound was measured by a travelling microscope with an accuracy of ± 1 μm.

3. Results and discussion

3.1. Metallography

Fig. 1 shows the scanning chart of intensities of $VK\alpha$ and $ZrL\alpha$ X-rays against distance determined by EPMA for the semi-infinite (pure V)–(pure Zr) couple diffused at 1273 K for 90 h. In the diffusion zone, formation of any intermetallic phase cannot be recognized. In the Zr-rich side a thick layer of the β-phase (about 400 μm) is formed quickly by the diffusion of vanadium in β-zirconium, but in the V-rich side penetration of zirconium is negligible. The concentration of vanadium in the β-phase at the interface of the phase boundary is about 5 at% which is less than 12 at% vanadium, the solubility of vanadium in the β-phase at 1273 K. However, the concentration of zirconium in the γ-phase at the interface of the phase boundary is identical with the solubility of zirconium in the γ-phase. This is due to the extremely faster diffusion of vanadium in β-zirconium [5] than that of zirconium in vanadium [6]. It takes much time before the concentration of vanadium in the β-phase at the interface of the phase boundary approaches the value predicted by the equilibrium phase diagram and subsequently nucleation of the intermetallic phase V_2Zr begins. At 1273 K, the lowest temperature in the present experiment,

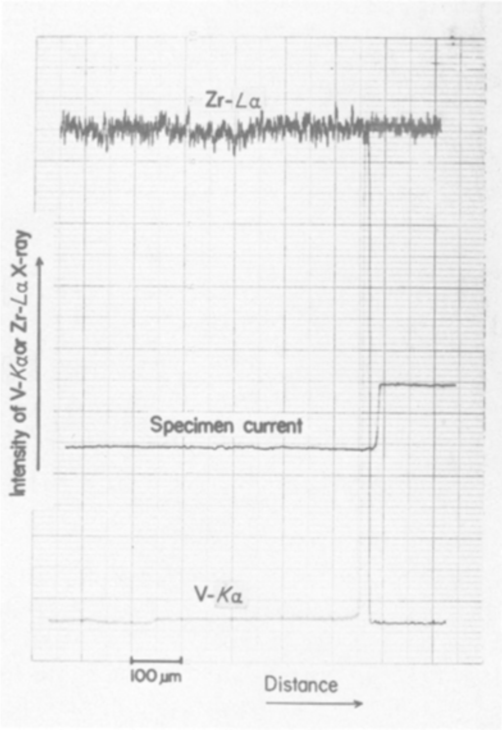

Figure 1 Scanning chart of intensities of V$K\alpha$ and Zr$L\alpha$ X-rays plotted against distance determined by EPMA for (pure V)–(pure Zr) couple diffused at 1273 K for 90 h.

formation of the V_2Zr phase cannot be recognized in the semi-infinite (pure V)–(pure Zr) couple even if it is diffused for as long a time as 500 h. However, above 1373 K, formation of the V_2Zr phase has been observed in a couple diffused for a time less than 300 h. Figs. 2 and 3 show optical micrographs of a semi-infinite (pure V)–(pure Zr) couple diffused at 1473 K for 50 and 230 h, respectively. In Fig. 2, only the V_2Zr layer is observed, while in Fig. 3, in addition to the V_2Zr phase, another phase unexpected from the equilibrium phase diagram of the V–Zr system is observed. This is identified by EPMA with the equiatomic VZr phase, as shown in Fig. 4. The compositions of the V_2Zr and VZr phases are found to be stoichiometric and independent of the diffusion time. The concentration fluctuation in the β-phase observed in Fig. 4 may be attributed to the grain-boundary diffusion, because the grain size of the β-phase is very small (50 to 100 μm), as can be seen in Fig. 3. In such regions of the concentration fluctuation, enhanced growth of the intermetallic compounds is recognized. It is noted that the layer of the VZr phase has been formed only at 1473 K, the highest temperature in the present experiment, by diffusing for more than 230 h. The VZr phase appears to be a metastable phase like the ω-phase which is known as the metastable phase in titanium- and zirconium-base alloys. In Zr-rich Zr–V [11], Zr–Mo [12] and Zr–Cr [13] alloys formation of the ω-phase has been confirmed after quenching them from the β–phase. A large vacancy flux in the diffusion couple produced due to the extremely large difference in the diffusivities of vanadium and zirconium atoms in the β-phase may be responsible for the formation of the defective and metastable ω-phase during a prolonged diffusion. The phase diagram of the V–Zr system is very similar to those of other zirconium-base binary systems, such as Cr–Zr, Mo–Zr and W–Zr systems, where only one intermetallic compound M_2Zr (M = Cr, Mo or W) appears. Then, it is expected that the metastable equiatomic phase like VZr is formed also in these binary systems by prolonged reaction diffusion. In fact, in (pure Mo)–(pure Zr) couple

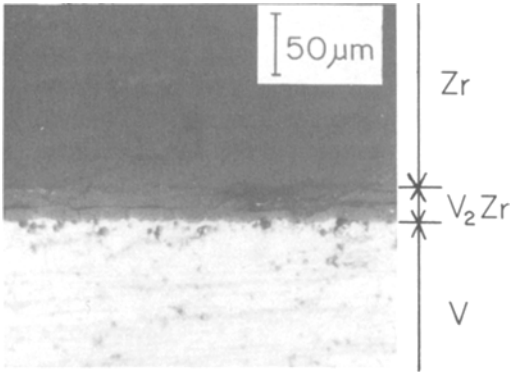

Figure 2 Optical micrograph of (pure V)–(pure Zr) couple diffused at 1423 K for 410 h.

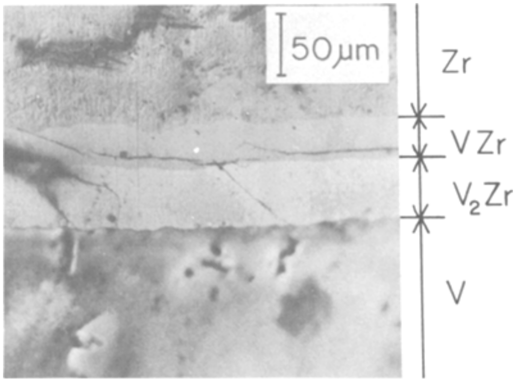

Figure 3 Optical micrograph of (pure V)–(pure Zr) couple diffused at 1473 K for 230 h.

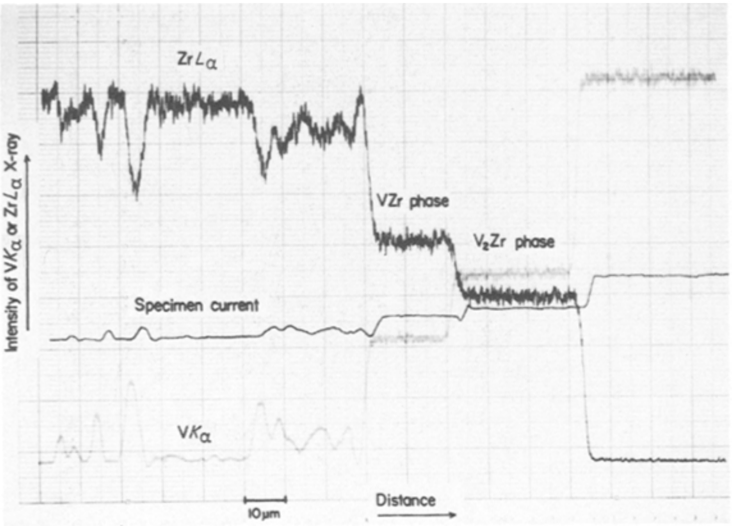

Figure 4 Scanning chart of intensities of V$K\alpha$ and Zr$L\alpha$ X-rays plotted against distance determined by EPMA for (pure V)–(pure Zr) couple diffused at 1473 K for 230 h.

diffusion at 1273 K for 113 h, formation of the metastable equiatomic phase MoZr has been recognized [14].

3.2. Growth kinetics of V_2Zr compound

Thickness, d, of the V_2Zr layer as a function of diffusion time, t, is plotted in Fig. 5. In the semi-infinite (pure V)–(pure Zr) couples, a temperature dependent incubation time is obviously required for the formation of the V_2Zr phase. As the diffusion temperature increases, the incubation time decreases. The predicted concentration of vanadium in the β-phase at the phase boundary by the equilibrium phase diagram is higher than that in the couple where formation of the V_2Zr phase cannot be recognized. To facilitate nucleation of the V_2Zr phase, use of the β-phase Zr–V alloy of high vanadium concentration instead of pure zirconium in the semi-infinite (pure V)–(pure Zr) couple may be effective, because the concentration of vanadium in the β-phase at the interface of the phase boundary can be saturated in the early period of the diffusion run. The concentration of the alloy, 13.5 at % vanadium, is a little less than the solubility of vanadium in the β-phase at 1473 K, 15.8 at % vanadium. For the same reason, use of a sandwhich type couple of pure zirconium foil inserted between two bulks of pure vanadium may also be effective. Then, in the present work, the sandwich type couples of (pure V)–(pure Zr foil of 50 to ~200 μm)–(pure V) have been also examined. Fig. 6 shows the time dependence of thickness, d, of the V_2Zr layer formed in the three types of couples diffused at 1473 K. The incubation time in the (pure V)–(Zr–13.5 at % V alloy) and (pure V)–(pure Zr foil of 50 μm)–(pure V) couples is remarkably shorter than that in the (pure V)–(pure Zr) couple. It has been observed

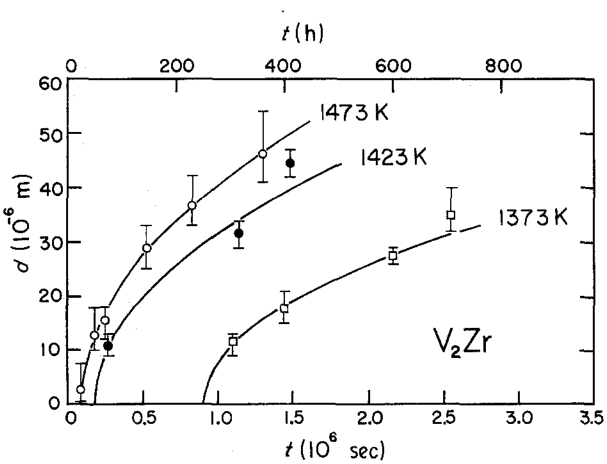

Figure 5 Growth of V_2Zr layer in (pure V)–(pure Zr) couples.

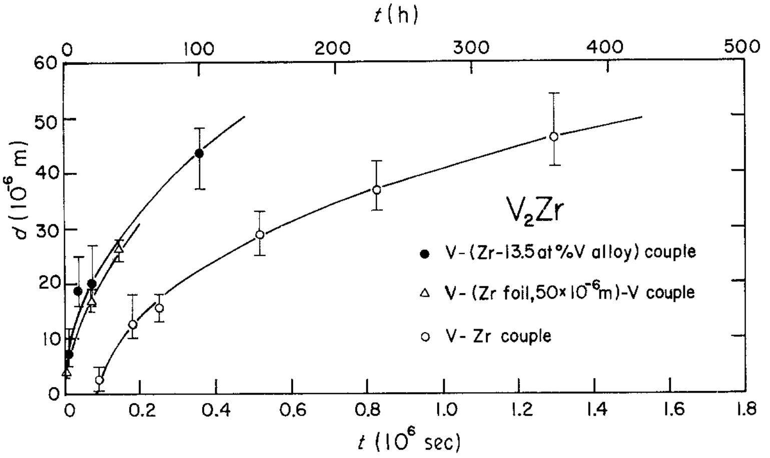

Figure 6 Growth of V_2Zr layer in (pure V)–(pure Zr), (pure V)–(Zr–13.5 at % V alloy) and (pure V)–(pure Zr foil of $50\,\mu m$)–(pure V) couples diffused at 1473 K. In Figs. 6, 7, and 8, the three types of couples are abbreviated as V–Zr, V–(Zr–13.5 at % V alloy) and V–(Zr foil, 50×10^{-6} m)–V couples, respectively.

that the thicker the initial foil of zirconium is, the longer the incubation time is.

For the reaction diffusion in the Fe–Ti system, formation of two intermetallic phase layers, Fe_2Ti and FeTi, is predicted from the equilibrium phase diagram [7]; however, no intermetallic phase has been formed in (pure Fe)–(pure Ti) couples [15]. Moreover, powder of Fe_2Ti or FeTi embedded in the interface of (pure Fe)–(pure Ti) couples has disappeared after the diffusion run. However, formation of the Fe_2Ti phase layer has been confirmed in (Fe–5 at% Ti alloy)–(Fe–80 at% Ti alloy) couples. Thus in the V–Zr system also, failure of formation of the intermetallic phase layer or delayed formation with an incubation time must not be due to the difficulty in nucleating the intermetallic phase, but due to the sluggish attainment of the concentration at the interface of the phase boundary to the nearly equilibrium concentration corresponding to that in the phase diagram.

As shown in Fig. 7, a linear relationship is observed between the square of thickness, d^2, of the V_2Zr layer and diffusion time, t, in all the couples and for all the diffusion temperatures. Thus, we have the equation,

$$d^2 = k^2 (t - t_0) \qquad (1)$$

where k is the rate constant and t_0 the incubation time. By extrapolating the plots in Fig. 7, the incubation times for the formation of the V_2Zr phase in the (pure V)–(pure Zr), (pure V)–(pure Zr foil of $50\,\mu m$)–(pure V) and (pure V)–(Zr–13.5 at% V alloy) couples diffused at 1473 K are estimated to be 24 and 1 h and nearly zero, respectively.

Fig. 8 shows the Arrhenius plots of k^2 against temperature for the V_2Zr layer in (pure V)–(pure Zr) and (pure V)–(Zr–13.5 at% V alloy) couples. Assuming the linearity of the plots in Fig. 8, the following Arrhenius equations can be obtained:

In the (pure V)–(pure Zr) couples,

$$k^2 = 1.1 \times 10^{-8} \times \exp(-190\,\mathrm{kJ\,mol^{-1}}/RT)\ \mathrm{m^2\,sec^{-1}} \qquad (2)$$

and in the (pure V)–(Zr–13.5 at % V alloy) couples,

$$k^2 = 1.8 \times 10^{-7} \times \exp(-210\,\mathrm{kJ\,mol^{-1}}/RT)\ \mathrm{m^2\,sec^{-1}}\ . \qquad (3)$$

In view of the limited number of the data points in Fig. 8, the activation energies for the growth of the V_2Zr layer in both types of couples appear to be consistent with each other. If an empirical relationship

$$Q = 140\,(\mathrm{J\,mol^{-1}\,K^{-1}})\,T_m \qquad (4)$$

between the activation energy, Q, for self-diffusion in pure metals [16] and the melting temperature, T_m, is applicable to the intermetallic compound V_2Zr (melting temperature: 1573 K), the activation energy for diffusion in V_2Zr is calculated to be $220\,\mathrm{kJ\,mol^{-1}}$, which is in agreement with the empirical value for the layer growth in Equations 2 and 3. Therefore, it is concluded that the thickening of the V_2Zr phase in these diffusion couples is diffusion-controlled.

It must be noted that a strange concentration–penetration profile has been found in some diffusion couples. Fig. 9 shows the scanning chart of intensities of V*Kα* and Zr*Lα* X-rays plotted against distance in the (pure V)–(pure Zr) couple diffused

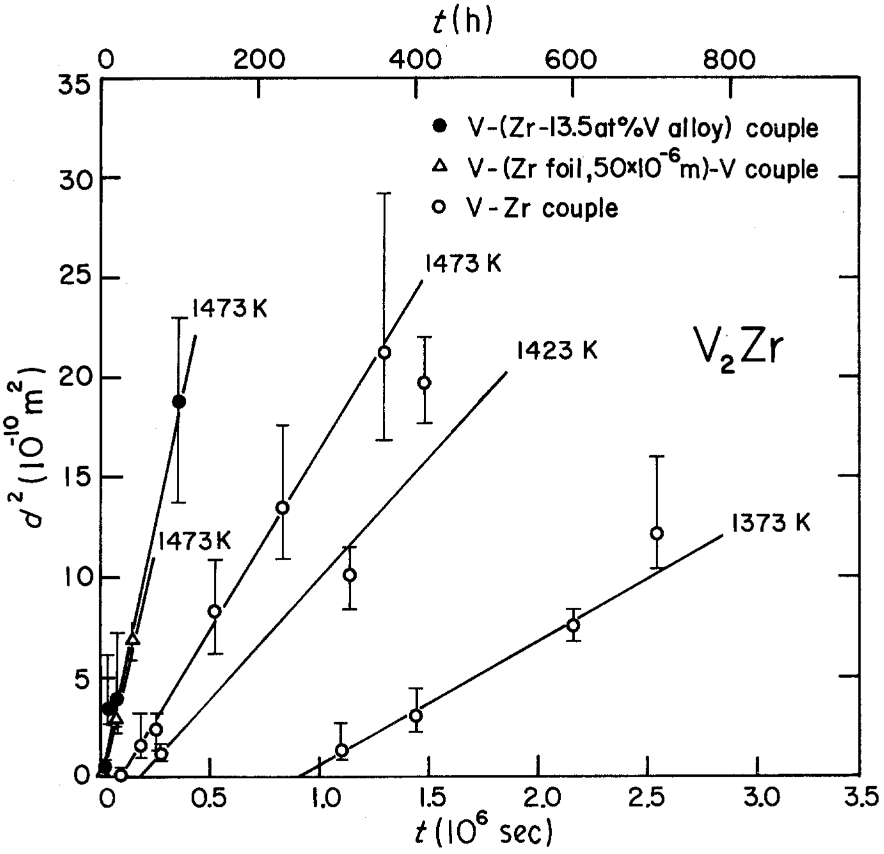

Figure 7 Plots of square of layer thickness of V_2Zr phase, d^2, against diffusion time, t.

at 1423 K for 410 h. A vanadium depleted zone of about 60 μm thick has been observed in the β-phase near the phase boundary. Beyond the depleted zone to the Zr-rich side, the concentration of vanadium is about 16 at %, in agreement with the solubility of vanadium in the β-phase at 1423 K. Fig. 10 also shows the depleted zone in the (pure V)–(Zr–13.5 at % V alloy) couple diffused at 1473 K for 20 h. In view of the fact that such a depleted zone has been frequently observed in the couple diffused at the lower temperatures, the following mechanism may be operative. Before

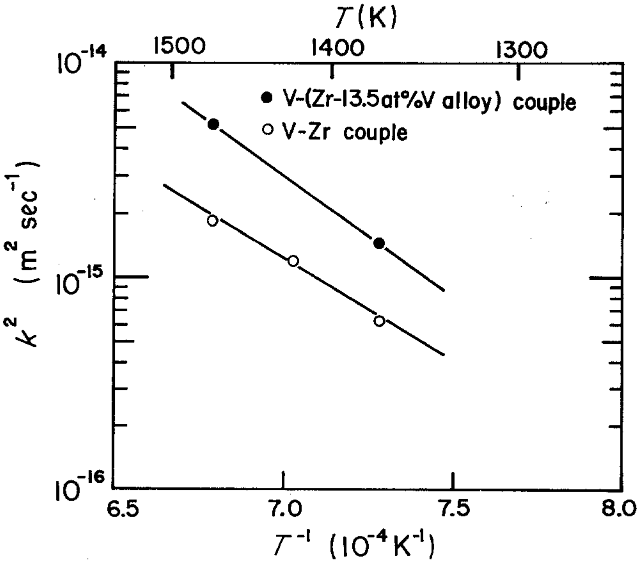

Figure 8 Temperature dependence of square of rate constant, k^2, for layer growth of V_2Zr phase in (pure V)–(pure Zr) and (pure V)–(Zr–13.5 at % V alloy) diffusion couples.

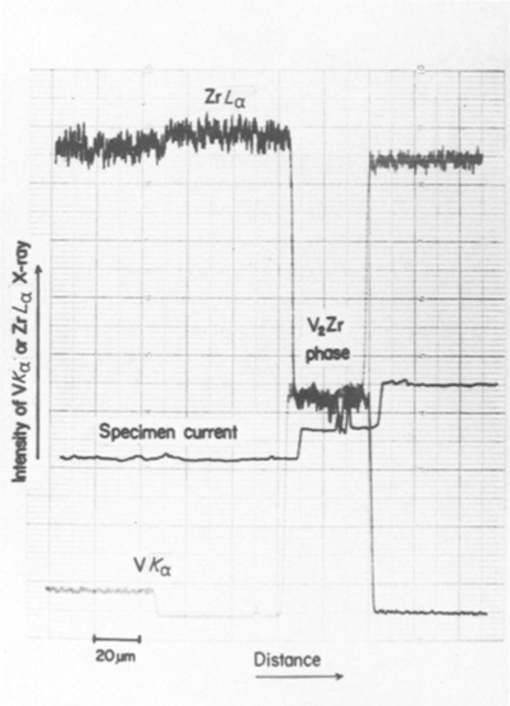

Figure 9 Scanning chart of intensities of V$K\alpha$ and Zr$L\alpha$ X-rays plotted against distance determined by EPMA for (pure V)–(pure Zr) couple diffused at 1423 K for 410 h.

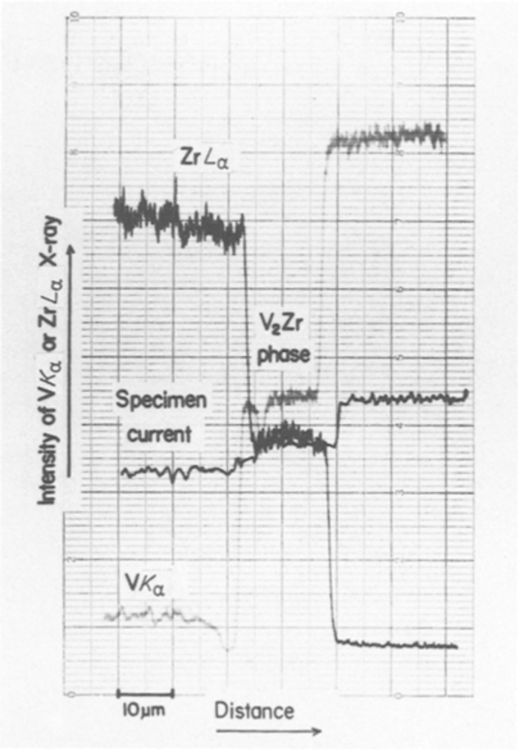

Figure 10 Scanning chart of intensities of V$K\alpha$ and Zr$L\alpha$ X-rays plotted against distance determined by EMPA for (pure V)–(Zr–13.5 at % V alloy). Couple diffused at 1473 K for 20 h.

the formation of the V_2Zr phase, a thick layer of the β-phase is formed, as shown in Fig. 1, then, the uphill diffusion of vanadium from the β-phase contributes in part to growth of the V_2Zr layer accompanied by the depleted zone in the β-phase. As described above, both the activation energy for the growth of the V_2Zr layer and the activation energy for diffusion in the V_2Zr phase are about 200 kJ mol^{-1}; on the other hand, the activation energies for self-diffusion of both components in the γ-phase are 370 to ~380 kJ mol^{-1} [6], which are much higher than that in the β-phase, about 100 kJ mol^{-1} [5]. This suggests that the supply of vanadium atoms from the β-phase is much easier than that from the γ-phase, then an uphill diffusion between the β-phase and the V_2Zr phase may be possible.

4. Conclusions

The experimental results from the present work on the reaction diffusion in the V–Zr system are summarized as follows:

1. in the (pure V)–(pure Zr), (pure V)–(Zr–13.5 at % V alloy) and (pure V)–(pure Zr foil of 50 μm)–(pure V) couples diffused in the temperature range 1373 to 1473 K, parabolic growth of the V_2Zr layer with respective incubation times is observed;
2. in addition to the V_2Zr phase, another phase VZr is formed in the (pure V)–(pure Zr) couple diffused at 1473 K for more than 230 h. The VZr phase appears to be a metastable phase like the ω-phase;
3. a vanadium depleted zone is observed in the β-phase near the phase boundary in the three types of couples diffused at the lower temperatures. This appears to be evidence for the uphill diffusion of vanadium from the β-phase which participates in growth of the V_2Zr layer.

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