Phase Diagram Imaging by Means of Temperature-Gradient Diffusion Couples

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1. Introduction

It is generally believed that, in diffusion couples, thermodynamic equilibrium between adjacent phase bands in established especially if the velocity of the phase boundary movement is slow [75Lag]. Romig and Goldstein [83Rom] showed that indications for disequilibrium as reported by Eifert et al. [68Eif] for Cu-Al interdiffusion couples are probably due to incomplete quenching of the specimens [87Not].

For several other systems, it has been reported [87Rom, 73Loo] that in no case has a significant difference between the composition of phases in diffusion couples and in equilibrated bulk alloys been observed. Hence, diffusion couples are appropriate tools for establishing portions of phase diagrams provided the high-temperature state can be "frozen" in by quenching, and the diffusivities of the components in the phases are such that the phase bands develop sufficient widths [62Kid] so that they are accessible for further investigation.

By combining the results from diffusion couples at several temperatures, the phase diagram in this temperature interval can be established. Obviously, the direct observation of equilibria involving three solid phases is not possible by this procedure. In order to investigate several phase equilibria in a temperature interval simultaneously and to make nonvariant reactions (formation and decomposition of phases) observable, it is necessary to introduce a temperature gradient parallel to the diffusion bands [91Len]. Such diffusion couples are termed temperature-gradient diffusion couples (TGDCs).

This experimental technique proved particularly successful for the reassessment of a portion of the Ti-N phase diagram for which prior investigations yielded contradictory results. The region between the $\delta$TiN$_{1-x}$ phase and the solid solution of nitrogen in $\alpha$Ti has been under discussion for several years: $\epsilon$Ti$_2$N, for instance, forms very rapidly during cooling. If this effect is disregarded and quenching is not deemed necessary, the presence of the $\epsilon$Ti$_2$N phase is not a valid basis for conclusions about the thermal stability of this phase. Not recognizing this fact has in the past led to erroneous results. Furthermore, two high-temperature phases have been reported, but their integration into the phase diagram with respect to their exact compositional and thermal stability regions has not been possible due to the scatter in the experimental results [91Len].

2. Experimental

Binary diffusion couples where one component is gaseous and the other a metal can sometimes be prepared simply by heating the metal in the atmosphere of the gaseous component. Nitrogen reacts readily with titanium, resulting in a $\delta$TiN$_{1-x}$ phase, which forms an excellent interface with the bulk titanium.

2.1 Isothermal Diffusion Couples

Isothermal diffusion couples were prepared at temperatures between 1050 and 1320 °C by heating 1-mm-thick Ti foil (typically 10 × 10 mm) in purified nitrogen atmosphere. This involved durations of treatment between 2 to 14 days. This preparation was performed in a cold-wall reactor with a tungsten heater and molybdenum radiation shields. In this reactor, it was not possible to quench the couples as rapidly as needed. To overcome this difficulty, the diffusion couples were wrapped in molybdenum foil and introduced into evacuated and Ar-backfilled silica tubes, which in turn were placed in a temperature-controlled furnace to reestablish equilibrium conditions. This additional heat treatment was performed for 2 h at

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1320 °C and up to 2 days for temperatures down to 1050 °C. After this treatment, the samples were quenched in water.

2.2 Temperature-Gradient Diffusion Couples

The preparation procedure for the samples destined for thermal gradient annealing was identical to that described for the isothermal diffusion couples. The samples had an elongated geometry of typically 10 to 20 x 2 x 1 mm. Several samples of this type were wrapped in Mo foil in a staggered double row fashion. The total arrangement had a length of 50 to 70 mm. The array was placed into evacuated and Ar-backfilled silica tubes and introduced into the heating zone of a furnace with a temperature gradient of 10 to 40 °C/cm. The temperature profile was measured before and after heat treatment. The annealing periods were identical to those for the isothermal couples. Details of this technique are given elsewhere [91Len1, 91Len2].

2.3 X-Ray Diffraction

For phase identification, isothermal diffusion couples were embedded in cold-setting resin in such a way that the nitride layers parallel to the surface could be successively removed by grinding with a diamond disk. An X-ray diffractogram with Ni-filtered CuKα radiation was taken after removal of every 10 to 15 μm. TGDCs could not be investigated by this technique since the phase band sequence may change within one sample, which may give rise to ambiguous XRD results. However, as shown only recently [92Ull1], microdiffraction techniques such as the Kossel technique can help to identify the phase band sequence even in very small regions. Thus this technique may also be suitable for establishing phase band sequences in TGDCs as a function of temperature.

2.4 Electron Probe Microanalysis

EPMA was carried out on isothermal and temperature-gradient diffusion couples. External as well as internal standardization was performed using titanium nitride phases. Details are presented elsewhere [92Len].

2.5 Differential Thermal Analysis

DTA was carried out up to 1350 °C. Alumina crucibles were used as sample containers. About 100 mg of coarsely powdered sample material was used for each run. The reference material was Ni. Heating under highly purified Ar was done at a rate of 5 °C/min.
3. Results and Discussion

Depending on the annealing temperature, in isothermal Ti-TiN diffusion couples, five different layer sequences of titanium nitride phases could be observed in the temperature interval 1050 to 1320 °C. These layer sequences could be identified using XRD. Figure 1a-e shows the metallographic microstructures of these couples. Rapid quenching of the diffusion couples was particularly important in order to retain the diffusion bands of the high-temperature phases $\eta Ti_3N_2-x$ and $\zeta Ti_4N_3-x$. Five isothermal sections of the phase diagram can be constructed from these couples, but it is impossible either to un-
Fig. 3 Results of DTA (heating cycle; run 1: first cycle, run 2: second cycle) of two bulk samples containing 29 and 31 at.% N, respectively. A shouldered DTA peak could be observed at 29 at.% N, reflecting the three nonvariant phase reactions shown in TGDCs in Fig. 2a and b.

ambiguously decide which phases are involved in the phase reactions or to obtain their nonvariant temperatures.

On the other hand, TGDCs near the expected nonvariant temperatures led directly to the nonvariant temperatures of the various three-phase equilibria and the phases involved. Two microstructures of temperature-gradient diffusion couples are shown in Fig. 2a and b. The layer sequence at the lower-temperature end of the couple shown in Fig. 2a is $\alpha$Ti(N)/$\varepsilon$Ti$_2$N/$\delta$TiN$_{1-x}$, and at the high-temperature end $\alpha$Ti(N)/$\eta$Ti$_3$N$_{2-x}$/\zeta$Ti_4$N$_{3-x}$/\delta$TiN$_{1-x}$. The onset of the appearance of $\eta$Ti$_3$N$_{2-x}$, which represents the nonvariant reaction:

$$\alpha$$Ti(N) + $\varepsilon$Ti$_2$N $\rightarrow$ $\eta$Ti$_3$N$_{2-x}$  \hspace{1cm} \text{(Reaction 1)}$

could be located at 1066 °C. In Fig. 2b, two nonvariant reactions are shown. At 1078 °C, the layer sequence changes from $\alpha$Ti(N)/$\eta$Ti$_3$N$_{2-x}$/$\varepsilon$Ti$_2$N/$\delta$TiN$_{1-x}$ to the five-layer sequence $\alpha$Ti(N)/$\eta$Ti$_3$N$_{2-x}$/\zeta$Ti_4$N$_{3-x}$/$\varepsilon$Ti$_2$/$\delta$TiN$_{1-x}$ (appearance of $\zeta$Ti$_4$N$_{3-x}$) representing the nonvariant reaction:

$$\eta$$Ti$_3$N$_{2-x}$ + $\varepsilon$Ti$_2$N $\rightarrow$ $\zeta$Ti$_4$N$_{3-x}$  \hspace{1cm} \text{(Reaction 2)}$

At 1080 °C, this five-layer sequence changes into a four-layer sequence $\alpha$Ti(N)/$\eta$Ti$_3$N$_{2-x}$/$\zeta$Ti$_4$N$_{3-x}$/$\delta$TiN$_{1-x}$ (disappearance of $\varepsilon$Ti$_2$N) corresponding to the nonvariant reaction:

$$\varepsilon$$Ti$_2$N $\rightarrow$ $\zeta$Ti$_4$N$_{3-x}$ + $\delta$TiN$_{1-x}$  \hspace{1cm} \text{(Reaction 3)}$
Section I: Basic and Applied Research

The TGDC technique allows a relative temperature resolution of better than 1 °C; the absolute accuracy is about ±5 °C and depends on the thermocouples used and the applied temperature gradients [91Len1].

The advantages of the TGDC technique are even more obvious when the results are compared with DTA results. In Fig. 3, DTA measurements of arc-melted and equilibrated bulk samples with gross nitrogen concentrations of 29 and 31 at.% N, respectively, are shown. A shouldersed DTA peak could be observed in the most favorable cases, where the shoulder obviously corresponds to Reaction 1 and the maximum of the peak corresponds to the coinciding peaks of Reactions 2 and 3. The second peak cannot be resolved any better because of the very small temperature difference.

Apart from the direct information about the nature of the phases involved in a phase reaction gained through their metallocraphic appearance and XRD peak pattern, the temperature information of the TGDC technique is substantially better. A combination of the described techniques (isothermal couples and TGDC, XRD, metallography) together with quantitative EPMA for measuring the composition of the phases in equilibrium have been used to construct a revised tentative portion of the Ti-N phase diagram, which is shown in Fig. 4. This diagram includes the high-temperature phases ηTi₂N₁₋ₓ and ζTi₄N₃₋ₓ which were overlooked at the time when the Ti-N phase diagram was compiled by Wriedt and Murray [87Wri].

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Cited References