JOURNAL OF SOLID STATE CHEMISTRY 91, 279–285 (1991)

The Temperature Gradient Diffusion Couple Technique: An Application of Solid–Solid Phase Reactions for Phase Diagram Imaging

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Received July 16, 1990; in revised form November 8, 1990

The conventional isothermal diffusion couple technique was modified by introducing a temperature gradient parallel to the diffusion bands. With this technique it is possible to study phase equilibria and phase reactions as a function of both temperature and composition simultaneously. Portions of the phase diagram are essentially direct projections of the observed microstructures ("phase diagram imaging"). With the aid of microprobe techniques, an accurate determination of compositions of coexisting phases is possible. The features of this technique are discussed for portions of the Ti–N system and several further applications are suggested. © 1991 Academic Press, Inc.

1. Introduction

Binary diffusion couples have been used extensively for studying phase reactions to establish phase diagrams. The Eindhoven school has reported numerous results on metal–metal interdiffusion couples [e.g., (*1*)] and—to a lesser extent—of metal–nonmetal couples [e.g., (*2*)].

It has been proven that at the interface boundary between binary diffusion bands a state which can be regarded as thermodynamic equilibrium can be approached upon heat treatment [(*3*) and references therein]. Thus, with the development of microanalytical probes—especially electron probe microanalysis—this technique has become a powerful tool for determining homogeneity regions and two-phase fields of phases coexisting at the annealing temperature. The merit of the diffusion couple technique stems from the fact that a chemical gradient (activity gradient) which allows the simultaneous investigation of more than one thermodynamic equilibrium state is introduced. However, in the diffusion couple studies reported so far, only the composition across isothermally annealed diffusion couples (the latter represent a section through the phase diagram at the respective temperature) has been considered. The possibility of introducing an additional gradient—the temperature—to further increase the amount of observable phenomena has never been suggested. By introducing a temperature gradient, the usual two-dimensional representation of phase reactions—the phase diagram—is achieved. Figure 1 shows an example of the potential of temperature gradient diffusion couples for establishing phase equilibria and boundary compositions of coexisting phases—called phase diagram imaging.

If one component is gaseous and forms a

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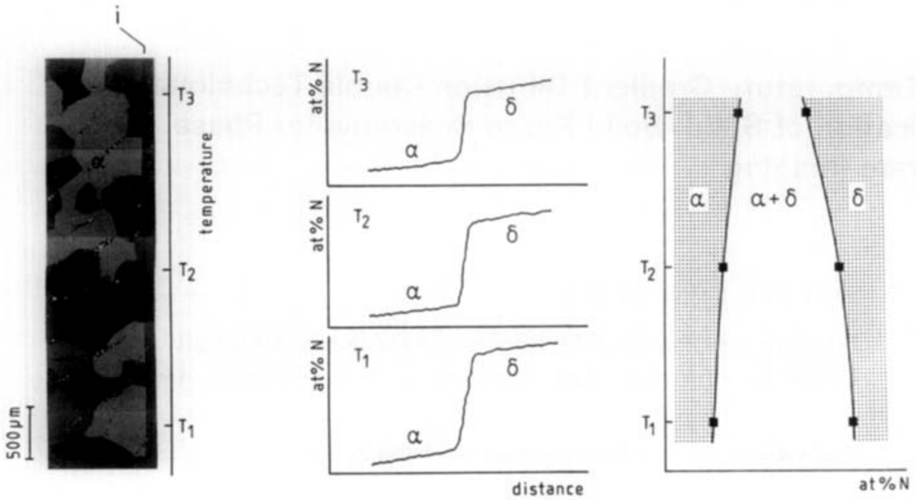

FIG. 1. Phase diagram imaging: From the microstructure of a TiN–Ti diffusion couple annealed in a temperature gradient (left) the microprobe scans (EPMA; middle) at the α/δ interface (i, left) yield a quantitative part of the two-phase field α-Ti(N) + δ-TiN_{1-x} (right). Hence, this sample can be translated directly into a portion of the phase diagram. An alignment of several samples (Fig. 3) yields a correspondingly larger portion of the phase diagram.

stable solid phase with the other component, the use of gas–solid reactions is—under certain conditions such as the formation of even diffusion fronts, negligible grain boundary diffusion, or negligible pore formation—the easiest way to prepare diffusion couples. For this *in situ* formation of diffusion couples no experimental difficulties arise; an intimate contact of the components is easily achieved to make material exchange possible. For the present case of the titanium–nitrogen system diffusion couples can be regarded as metal nitride–metal (TiN–Ti) couples rather than nitrogen–metal (N_2–Ti) couples since only the solid phases are considered here.

The subnitride region of the Ti–N system has been under discussion for several years: Since the rapid formation of ε-Ti_2N was not realized, quenching had not been regarded as necessary, and the reported decomposition temperatures for ε-Ti_2N scattered over more than 1000 K (*4*). Furthermore, the existence of two high-temperature phases was reported (*5*, *6*).

To supply the basic information the results obtained with arc-melted and quenched specimens are plotted (Fig. 2). The results represent more an experimental summary of XRD results vs. composition and quenching temperature than a portion of a phase diagram (*7*): the phase reactions could not be determined due to sample inhomogeneities, which constitute the most restrictive factor for this technique.

Because of the narrow composition and temperature region in which the titanium subnitride phases coexist, the successful determination of these phase reactions with the temperature gradient diffusion couple technique should be a proof for the method's applicability. The experimental technique is the subject of the present study which includes examples for the Ti–N system. Details of the Ti–N system together with a literature review will be published elsewhere.

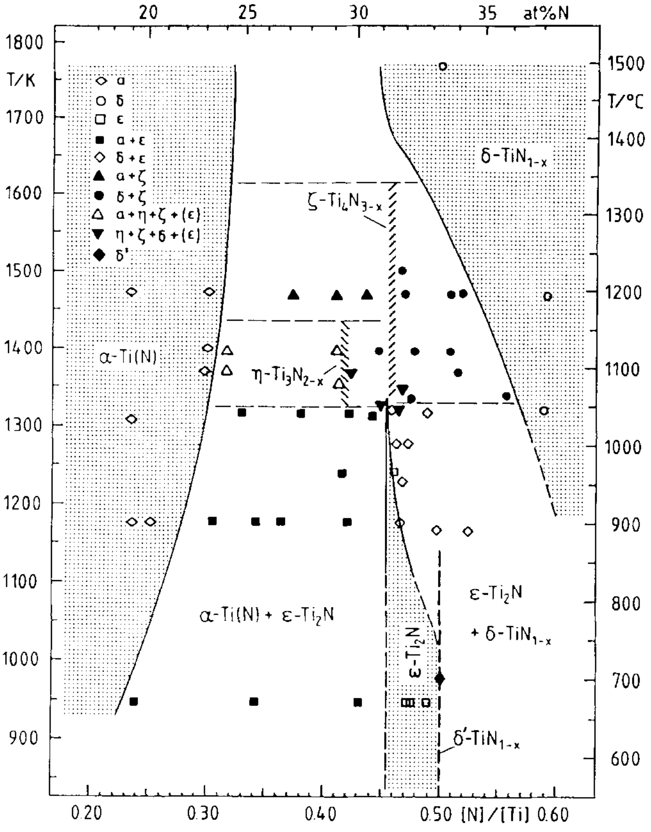

FIG. 2. Results obtained by arc-melting and quenching of buttons for the subnitride region of the Ti–N system (7). The true phase relationships could not be determined.

2. Experimental

2.1 Prepreparation of Diffusion Couples

Titanium sheets of various dimensions (typically 1 mm thick) were heated in high-purity nitrogen atmosphere with the usual precautions to avoid oxygen and water vapor contamination. During heating a gold-colored δ-TiN_{1-x} layer formed at the surface. For metallographic preparation and development of the diffusion layers a minimum thickness of the outer δ-TiN_{1-x} layer of about 100 μm was sufficient. This involved for example heating times of 14–21 days at around 1420 K and 5 days at around 1620 K. After these periods the core of the sample consisted of α-Ti(N). Depending on the temperature, between the δ-TiN_{1-x} surface and the core, three subnitride phases (η-Ti_3N_{2-x}, ζ-Ti_4N_{3-x}, ε-Ti_2N) can occur, having compositions between 29 and 33 at% N (see Fig. 2). After heat treatment the samples were cooled to room temperature within about 2 min. Because of the rapid formation of ε-Ti_2N the samples so-obtained contained—independent of heating temperature—an ε-Ti_2N layer between δ-TiN_{1-x} and α-Ti(N).

2.2 Temperature Gradient Annealing

In order to reestablish equilibrium conditions which can be frozen upon quenching,

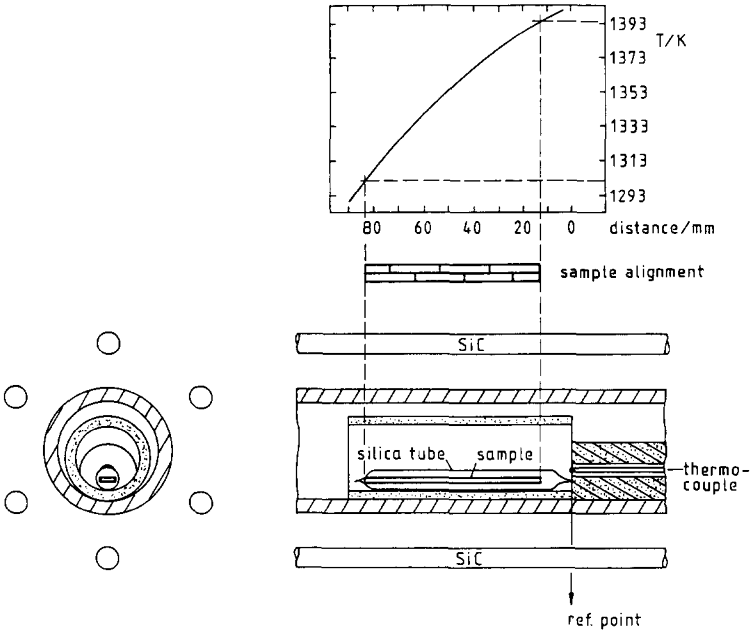

FIG. 3. Top, example for a temperature gradient in which the samples were annealed. Middle, alignment of samples. Bottom, schematic drawing of the SiC furnace used for temperature gradient annealing. Dotted and hatched areas, cut through the ceramic tubes which are the internal devices to adjust the samples.

the samples were aligned in 0.025-mm thick Mo-foil and sealed under Ar in silica tubes. They were then subjected to a heat treatment in a resistively heated SiC furnace (Fig. 3) in which the vertex temperature was automatically controlled. Before and after positioning the samples in the furnace the temperature gradient was measured by means of a thermocouple introduced in an empty silica tube with one end sealed, which was of the same size as the tube for heat treating the samples. Typical temperature deviations of the T vs distance curves before and after heat treatment were 1–3 K. The accuracy of positioning the samples was better than ±0.5 mm. A small systematic error in the temperature occurs since different thermal conductivities of the sample and the thermocouple wires exist. This error could not be corrected.

In order to keep conditions sufficiently near the equilibrium conditions established during prepreparation of the diffusion couples, the temperature interval of the gradient experiment was maximum ±50 K apart from the prepreparation temperature. Therefore for each gradient experiment at a separate temperature a separate prepreparation step had to be performed.

After 2–5 days of annealing in the temperature gradient the samples were quenched in water.

Metallographic preparation was performed by grinding with a diamond disk and subsequently polishing with diamond paste. Best results for inspection in polarized light were obtained by polishing the samples with an aqueous aluminum oxide suspension for a few minutes within the last step and avoiding any organic solvent.

3. Results and Discussion

As indicated in Fig. 1, a portion of the phase diagram can be obtained directly from the boundary compositions of two coexisting phases as determined by microprobe measurements and plotted as a function of temperature.

Figure 4 shows a microstructure from which the formation/decomposition of Ti–N subnitride phases can be observed. Besides the possibility of placing several microprobe scans at a corresponding constant temperature to directly plot the phase diagram, the formation/decomposition temperatures and hence the phase reactions can be determined in a quite straightforward manner. In particular, it can be seen that the bright ε-Ti_2N phase band vanishes at 1353 K. It should be noted that this represents one of the most direct recordings of the formation/decomposition temperature of a compound. Usually such measurements are performed using more "indirect" sources such as reaction enthalpies (DTA), high-temperature X-ray diffraction, or Knudsen-cell mass spectrometry, which may not have the same degree of sensitivity.

An internal check of the decomposition temperature can be performed by comparing the results of two opposite surfaces of the same sample which correspond to the same temperature. Nearly identical temperature values indicated that grain boundaries do not substantially influence the results. This is especially true for the formation/decomposition of the ε-Ti_2N phase, where this (relative) error was well below ±1 K.

In other cases such as for the decomposition of ζ-Ti_4N_{3-x} it was observed that near the phase's decomposition temperature the phase band vanishes where a grain boundary of the α-Ti(N) core is met. This is probably due to the close structural relationships of the phases and the formation mechanism involved [shearing of lattice planes (*7*)], which may influence the determined critical temperatures. However, since the grain size is relatively small as compared to the applied temperature gradient (compare Fig. 1 and 3) the differences observed for opposite surfaces were less than 2 K. The absolute accuracy of the measurement using standard Pt/PtRh-thermocouples was within ±3 K (determined from a comparison of several thermocouples at the same temperature) and the error arising from sample positioning was, depending on the gradient, about 1 K.

Problems may arise for systems where optical differentiation is difficult. For the present case polarized light was suitable for observation of the ε-Ti_2N phase. The differentiation of the two phases η-Ti_3N_{2-x} and ζ-Ti_4N_{3-x} (which both occur in the vicinity and above the decomposition temperature of ε-Ti_2N) was more difficult since the appearance in polarized light is less intense and both have a very similar hatched texture. However, with sample rotation in polarized light and increased light intensity the interface of η-Ti_3N_{2-x} and ζ-Ti_4N_{3-x} could be detected in most cases.

With the application of this technique the most complicated portion of the phase diagram of the Ti–N system could for the first time be established. It was possible to determine the true phase diagram from a choice of three different proposals consistent with the results from isothermal diffusion couples (*8*). As one of the most important results the presence of two nonvariant three-phase equilibria (η-Ti_3N_{2-x} + ζ-Ti_4N_{3-x} + ε-Ti_2N and ζ-Ti_4N_{3-x} + ε-Ti_2N + δ-TiN_{1-x}), which exist only 2 K apart from each other, could be detected (*8*). It seems impossible to obtain this information by the conventional isothermal diffusion couple technique.

4. Further Possibilities for Applying the Temperature Gradient Diffusion Couple Technique

This temperature gradient diffusion technique is apparently applicable not only for

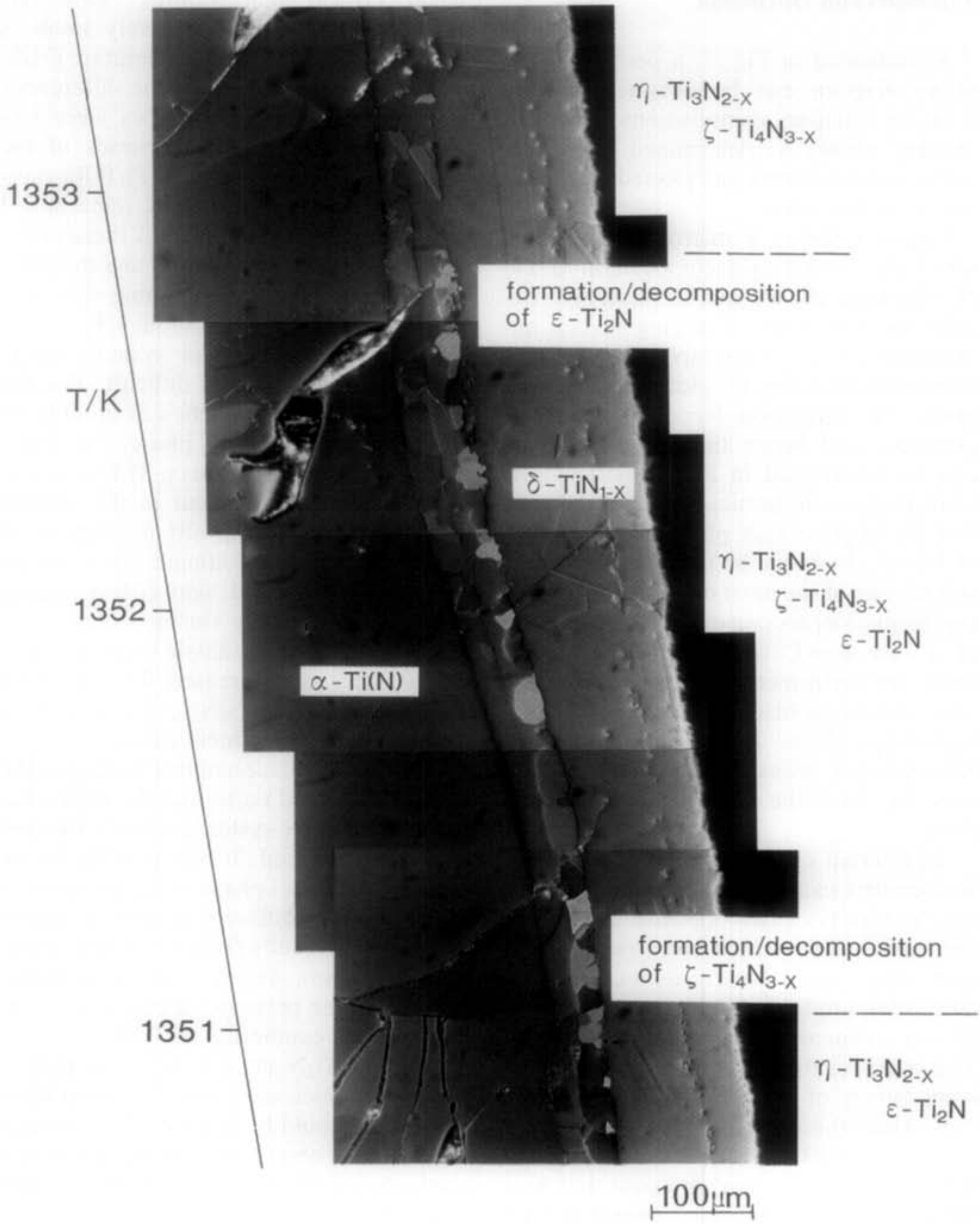

FIG. 4. Temperature gradient diffusion couple directly showing the phase reactions in a portion of the Ti–N system. Temperature gradient about 24 K/cm. The existing phase bands between α-Ti(N) and δ-TiN_{1-x} at the respective temperatures are given on the right margin. ε-Ti_2N decomposes at 1353 K (phase reaction: ε-$Ti_2N \rightarrow \zeta$-$Ti_4N_{3-x} + \delta$-TiN_{1-x}). Slightly above 1351 K the phase reaction η-$Ti_3N_{2-x} + \varepsilon$-$Ti_2N \rightarrow \zeta$-$Ti_4N_{3-x}$ could be detected.

the determination of formation/decomposition temperatures of phases, homogeneity regions, and extensions of two-phase fields as a function of temperature as shown above, but also seems to be applicable to order–disorder studies. The order–disorder transition of a compound is usually a function of composition and temperature. The investigation of this transition temperature for different compositions of the same compound is extremely time consuming and has generally not been performed. With the present technique however (not necessarily to be performed in a silica tube), a single temperature gradient diffusion couple can reveal the ordering temperature as a function of composition, provided that a specific property is obtainable from the polished surface (polarized light, etching behavior). Furthermore, probe measurements should make it possible to distinguish between first- and second-order transitions (the presence or absence of a composition jump).

For transition metal–nitrogen systems there are already numerous applications to clarify previousy unresolved points [e.g., order–disorder transitions in the systems Ti–N (δ-TiN_{1-x} → δ'-TiN_{1-x}), Nb–N (δ-NbN_{1-x} → γ-Nb_4N_{3-x}), Mo–N (γ-MoN_{1-x} → β-Mo_2N), and V–N (δ-VN_{1-x} → δ'-VN_{1-x}) and phase reactions of subnitride phases in all transition metal–nitrogen systems].

The modification of the experimental setup to include special (high-temperature, high-pressure) furnaces, accurate (optical) temperature measurements, and/or an improved quenching procedure (if necessary) as well as investigations of appropriate temperature and composition gradients will certainly improve this technique.

5. Conclusion

The introduction of a temperature gradient during annealing of solid–solid diffusion couples for the so-called phase diagram imaging has shown very encouraging results. It was possible to clearly establish the phase equilibria in the Ti–N system in a region where several phases occur and where nonvariant three-phase equilibria are only 2 K apart. Since this temperature gradient diffusion couple technique has been successful for a quite complicated system, it should also be applicable for most other solid–solid diffusion studies dealing with the measurement of critical temperatures, the investigation of order–disorder transitions, and the establishment of phase diagrams.

Acknowledgments

The author thanks Professor Dr. Peter Ettmayer for his supportive interest and many valuable discussions throughout this study. Thanks are also due to Mrs. Cathryn Jelinek for her help with the preparation of the manuscript. This work was supported by the Austrian Science Foundation FWF under Project 7370.

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