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The diffusion couple technique in phase diagram determination

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Abstract

The diffusion couple technique is a valuable experimental approach in studying phase relations in multicomponent systems. The use of different modifications of the method is illustrated by examples of phase diagram determination in various ternary systems. It is also shown that a number of error sources may appear when multiphase diffusion experiments are employed for constructing isothermal cross-sections. The difficulties connected with the concentration measurement at the interfaces and problems associated with the formation of a quasi-equilibrated diffusion zone are discussed. It is demonstrated that the efficiency of the diffusion couple technique is very high. However, in order to increase the reliability of the information obtained about a ternary diagram, a combination of the diffusion methods with an investigation of selected alloys is desirable.

Keywords: Phase equilibria; Diffusion couple; Electron probe microanalysis

1. Introduction

Phase diagrams play an important role in the understanding of many scientific and technological disciplines, and are important guidelines in the production, processing and application of materials. It is, therefore, not surprising that substantial efforts have been given to developing experimental and theoretical methods of establishing phase relations in multicomponent systems. Phase equilibria in rather complex systems may now be calculated with a certain degree of confidence. However, in the near future, the theoretical assessments will likely remain a complementary tool only and not a replacement for experiment. In the present paper, we shall be concerned with one of the experimental techniques frequently used in phase diagram investigations, namely a diffusion couple method.

Although the idea to use diffusion couples for constructing phase diagrams was suggested at least four decades ago [1], no comprehensive treatment of this subject (in a form suitable not only for specialists, but also for undergraduates) is available yet. Therefore, we would like to discuss mainly in a qualitative way the relation between multiphase diffusion phenomena on the one hand, and the topology of a phase diagram on the other hand. This article is an attempt to provide the reader with a framework for practical application of the diffusion couple technique as a 'research tool' in various fields of solid state chemistry and materials science.

The available body of experimental work is now sizable enough to recommend limitation of this survey paper to the non-ionic materials, i.e. mainly to metals. Readers interested in the field of the ionic solids are referred to the recent general textbook of Schmalzried [2].

We will illustrate most of the basic ideas by examples of phase diagram determination in actual material systems. Throughout the paper, reference has been made to our original publications upon which much of the text is based. By reading these original articles one gains a broader understanding and clear insight into the finer nuances of the diffusion couple method.

The present paper may be looked upon, then, as a summary of the authors' experience in this research field and we take great pleasure in dedicating it to the memory of Alan Prince, a man who showed so much courage and determination in pursuing his professional goals.

2. General principles of the diffusion couple method

The use of diffusion couples in phase diagram studies is based on the assumption of local equilibria in the diffusion zone. The latter implies that each infinitely thin layer of such a diffusion zone is in thermodynamic equilibrium with the neighbouring layers. In a translated sense, this means that chemical potential (activity) of species varies

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continuously through the product layers of the reaction zone and has the same value at both sides of an interface.

This concept of local equilibrium being attained at interfaces plays a prominent role in the diffusion theory. It is to be remarked, however, that since diffusion takes place only by virtue of a thermodynamic potential gradient, any system in which diffusion occurs is not at equilibrium. In other words, for a phase boundary to migrate (i.e. for a reaction product to grow) within the diffusion zone there must be a free energy difference (driving force) which implies some deviation from equilibrium. Throughout this discussion, we suppose that local equilibrium is maintained in the diffusion zone, which means that reaction is very rapid compared with the rate of diffusion.

It may be recalled that a diffusion-controlled interaction in a multiphase binary system will invariably result in a diffusion zone with single-phase product layers separated by parallel interfaces in a sequence dictated by the corresponding phase diagram. The reason for the development of only straight interfaces with fixed composition gaps follows directly from the phase rule. Three degrees of freedom are required to fix temperature and pressure and to vary the composition. Reaction morphologies consisting of two-phase structures (i.e. precipitates or wavy interfaces) are, therefore, thermodynamically forbidden, assuming that only volume-diffusion takes place.

In a ternary system, on the other hand, it is possible to develop two-phase areas in the diffusion zone because of the extra degree of freedom. The diffusion zone morphology, which develops during solid-state interaction in a ternary couple, is defined by type, structure, number, shape and topological arrangement of the newly formed phases. The resulting microstructure of the reaction zone can be visualized with the aid of the so-called *diffusion path*. This is a line on the ternary isotherm, representing the locus of the average composition in planes parallel to the original interface throughout the diffusion zone. Naturally, the diffusion path in a ternary system must fulfil the law of conservation of mass. If no material is lost or created during the interaction, then the diffusion path is forced to cross the straight line between the end-members of the reaction couple (so-called mass balance line) at least once.

If phases are separated by planar interfaces, the diffusion path crosses the two-phase region on the isotherm parallel to a tie-line and it can be assumed that local equilibrium exists along the whole interface. However, this is not necessarily the case: regions of supersaturation can be formed near the interfaces. A thermodynamically unstable structure will then be created which will give rise to wavy interfaces or isolated precipitates.

Kirkaldy and Brown [3] formulated a number of rules, which relate the composition of the reaction zone to the phase diagram. Later, these rules were conventionalized by Clark [4]. In recent years, the research in multicomponent diffusion took on a new lease of life, due primarily to the availability of computational power matching the complexity of the available algorithms. The reader seeking more information on this rather complex subject should access the relevant work of the research groups of Kirkaldy [5], Morral [6] and Ågren [7].

Referring for details especially to Ref. [4] we will just summarize here the main ideas, using a hypothetical reaction couple of an A–B–C-ternary system shown in Fig. 1.

For a given couple under conditions of chemical equilibrium the reaction path involves a time-independent sequence of intermediate layers. The plot gives information about the order of the product layers, their morphology and their compositions. For example, in the hypothetical system shown in Fig. 1, a solid line crossing a single phase field on the isothermal section (e.g. a–b) denotes an existing layer of that phase in the reaction zone of the couple A/Z. A dashed line parallel to a tie-line in a two-phase field (g–h) represents a straight interface between two single phases. A solid line crossing tie-line on the isotherm (b–c) represents a locally equilibrated two-phase zone (in fact, a wavy interface) in the couple. A solid line entering a two-phase field and returning to the same phase field (d–e–f) represents a region of isolated precipitates. A dashed line crossing a three-phase field (e.g. i–j or k–l) implies an interface in the diffusion structure with equilibrium between three phases, either a two-phase layer adjacent to a layer consisting of a different phase (e.g. i/j interface) or adjacent two-phase layers with one common phase (e.g. k/l interface).

Before we start to illustrate specific examples of phase diagram determination by means of diffusion couples, it is important to make some general comments concerning sample preparation and analytical techniques used in this method.

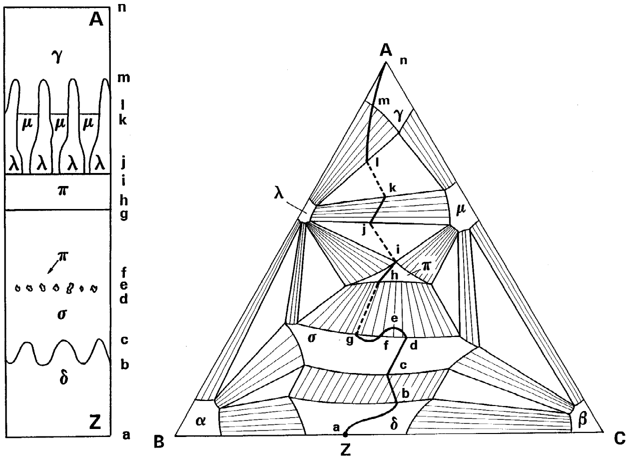


Fig. 1. A reaction zone structure in a hypothetical couple A/Z of the A–B–C system (on the left) and the corresponding diffusion path plotted on the isotherm of the ternary diagram (on the right). The low-case letters relate the structure to the appropriate composition on the isotherm. (Note: all paths in three-phase fields must be denoted by dashed lines, as a three-phase layer cannot form in a ternary diffusion couple.)

3. Experimental procedures

3.1. Preparation of diffusion couples

Several techniques are available to make solid-state diffusion couples, i.e. to bring two (or more) materials in such intimate contact that each diffuses into the other. In the most commonly used procedure, the bonding faces of the couple components are ground and polished flat, clamped together and annealed at the temperature of interest. Depending upon the initial materials, various ambient atmospheres can be used (e.g. vacuum, inert gas, etc.). After the heat treatment, quenching of the sample is desirable in order to freeze the high-temperature equilibrium.

For some metallic systems, different electrolytic and electroless plating techniques can also be utilized to fabricate diffusion couples. In this case, one half of the couple is typically a piece of a bulk alloy. The second half of the couple is formed by plating the second alloy onto the bulk alloy substrate.

Other plating techniques have also been employed including plasma spraying and chemical vapour deposition (CVD). These techniques are suitable for both metals and nonmetals. Thermal evaporation, electron beam evaporation, or laser evaporation can be used as well to deposit the second component layer onto a bulk substrate.

It is also possible to create a multiphase diffusion couple by annealing a substrate material in a reactive gas atmosphere [8]. Such experiments can be carried out in a conventional way (under isothermal conditions) or by imposing a temperature gradient perpendicular to the diffusion direction in the couple. The latter method enables one to observe competing phase reactions ‘simultaneously’ as a function of temperature [9].

3.2. Analytical techniques and specimen preparation

As explained earlier, in order to obtain information about the phase equilibria existing in a system at a specified temperature, the phase boundary concentrations within the diffusion zone have to be measured.

Different measurement techniques can be used to determine the chemical compositions on both sides of the interfaces. There are Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS), Rutherford backscattering spectrometry (RBS), glancing angle X-ray diffraction, electron probe microanalysis (EPMA) and analytical electron microscopy (AEM). In this paper we shall be concerned only with the last two methods, which are the most suitable for the investigation of ‘bulk’ diffusion couples. The others are used for determining composition depth profiles in studies of interdiffusion and reactions in thin-film couples.

The EPMA has been used since the early 1960s to measure concentration profiles in diffusion couples and has proven itself an indispensable tool in the determination of phase diagrams. There are literally hundreds of studies which employed this microanalytical technique. By contrast, the AEM became available for diffusion couple investigations somewhat later. Currently, the EPMA is a widely accepted technique for the analysis of phase relations in multicomponent systems. The complexities in specimen preparation and quantification of the results have prevented AEM from becoming a common method for diffusion couple studies. Nevertheless, these two techniques could form a powerful combination for the study of phase stability and reactive diffusion in solids.

In the EPMA high energy electrons are focused to a fine probe and directed at the point of interest in the diffusion couple. The incident electrons interact with the atoms in the sample and generate, among other signals, characteristic X-rays. These X-rays are detected and identified for qualitative analysis and with the use of suitable standards they can be corrected for matrix effects in order to perform quantitative analysis. In the EPMA bulk solid samples are investigated while the AEM is dealing with electron transparent thin films. Also the procedures used for X-ray quantification are quite different in both techniques.

The principal advantage of the EPMA is the ability to measure compositions of very small volumes of a specimen. The spatial resolution for bulk specimens is limited to ~1 μm. For thin foils, resolutions better than 50 nm are attainable routinely. Obviously, in order to obtain the most reliable results the operating conditions must be optimized. Accelerating voltage, beam current and counting time are, perhaps, the most critical parameters. The optimization of these parameters has been discussed in detail [10] and will only be summarized briefly here.

1. A ratio of operating accelerating voltage to excitation potential for the measured characteristic X-ray radiation of ~2–3 is desirable in order to maximize peak to background ratio and minimize the X-ray generating volume.
2. The value of beam current has to be chosen such that the X-ray counts are maximized for a statistically meaningful analysis without greatly increasing the electron beam size.
3. Counting times must be long enough to allow the accumulation of sufficient X-ray counts for statistically meaningful results (without producing too much carbon contamination).

Presently, two different techniques, wavelength dispersive spectrometry (WDS) and energy dispersive spectrometry (EDS) can be used to collect X-ray spectra from the samples being analyzed. Both systems have specific advantages and disadvantages and the choice will depend on the materials studied. In many modern instruments both types of spectrometers can be used simultaneously.

Some of the characteristics of these analytical systems, which are important with respect to quantitative analysis of diffusion couples include the following.

3.2.1. For WDS

1. Elemental detection for atomic numbers $Z \geq 4$.
2. X-ray energy resolution as good as 5 eV.
3. A high counting rate and low background which gives detectability limits of the order of 100 ppm.

Disadvantages: sequential detection and relatively high beam current necessary.

3.2.2. For EDS

1. Elemental detection for atomic numbers $Z \geq 11$ (in routine applications) or $Z \geq 6$ with windowless and ultra-thin detectors.
2. Maximum X-ray energy resolution ~140 eV at Mn Kα.
3. A low count rate and a low peak to background ratio compared with the WDS system. Detectability limits of the order of 1000 ppm are obtained with the EDS.

On the other hand: detection simultaneously!

For a very detailed account of the electron beam-based techniques the excellent book by Goldstein et al. [10] should be consulted.

3.3. Preparation of diffusion couple specimens for EPMA

As is the case in any microanalytical technique, specimen preparation is crucial. One must take care not to introduce into the experimental results any artefacts connected with the preparation of diffusion couple samples, which are to be analyzed with the EPMA.

Standard metallographic procedures can be used to prepare bulk multiphase couples for analysis by EPMA. The critical requirement is to prevent 'smearing' across the interphase interfaces. Good metallographic practice, and, perhaps, on some occasions a final electropolish may prevent contamination of a given phase from an adjacent area of the sample. In addition, special care has to be taken so that there are no apparent height differences between the components of the couple.

Once a suitable specimen has been prepared it can be analyzed by EPMA, and the measured concentrations can be used to define the end points of the tie-lines in the equilibrium phase diagram.

4. Variations of the diffusion couple technique

There are several variations of the diffusion couple method. In the first variant, the sample to be studied is a classical semi-infinite diffusion couple, which means that after the diffusion annealing the couple ends still have their original compositions. If volume diffusion in a semi-infinite couple is a rate-limiting step, local equilibrium is supposed to exist, in which case the rules described above can be used to relate the reaction zone morphology, developed during isothermal diffusion, to the phase diagram. The main feature of this variation of the diffusion couple method is that the phase composition of the reaction zone is independent of time and that the diffusion path is fixed. The versatility of this technique in constructing isothermal cross-sections of ternary systems has been demonstrated repeatedly (see e.g. Refs. [11–14]).

It is often necessary to investigate couples with end-members of various compositions in order to get all the information needed to find the phase relations at the annealing temperature. However, the necessary number of samples can be decreased appreciably by using polyphase terminal materials in diffusion couples. In the case of the study of, for instance, a ternary system, the chance 'to hit' interfaces at which three phases are in equilibrium, is much larger when two-phase alloys are used as end-members. Schematically this procedure is shown in Fig. 2. If a diffusion couple between P and Q is assembled, the reaction zone after annealing at a specified temperature might exhibit the morphology indicated in Fig. 2b. In area 1, microprobe measurements will reveal the three-phase equilibrium $\alpha+\mu+T$, whereas from area 2 the equilibrium triangle $\beta+\gamma+T$ existing on the isotherm can be found.

Application of this technique can be demonstrated by an example of studying phase relations in the ternary Ag–Fe–Ti system at 850°C [15]. This system is of considerable practical importance because Ag–Ti alloys are widely used as active filler metals for brazing steel components.

Interaction between an equilibrated two-phase alloy with the nominal composition $Fe_{30}Ti_{70}$, consisting of FeTi intermetallic and β-Ti (with nearly 18 at.% of Fe) and Ag at 850°C leads to the formation of the two-phase layer TiAg+FeTi in the diffusion zone (Fig. 3a). Two interfaces where three phases exist in equilibrium are found. The TiAg-matrix is in equilibrium with both β-Ti (with ~14.5 at.% of Fe and 2.0 at.% of Ag) and FeTi, which is a constituent of the starting two-phase alloy. The solubility of iron in the TiAg-matrix is negligible and the solubility of silver in the FeTi is estimated as ~0.5 at.%. This two-phase reaction layer also adjoins the Ag-based solid solution. The observed morphology indicates the existence of the three-phase equilibria FeTi+TiAg+Ag and FeTi+TiAg+β-Ti on the isotherm.

When a two-phase $Ti_{80}Ag_{20}$ alloy containing after equilibration the Ti_2Ag-intermetallic and α-Ti, is used as end-member of the diffusion couple, the reaction with Fe at this temperature results in the formation of continuous layers of the binary compounds Fe_2Ti and FeTi (Fig. 3b). The micrograph in Fig. 3b shows only a part of the diffusion zone close to the Fe/reaction product interface. The original end-member, composed of α-Ti and Ti_2Ag, is much further away from the interface (about 500 μm). Deeper in the alloy, a two-phase layer β-Ti and TiAg was

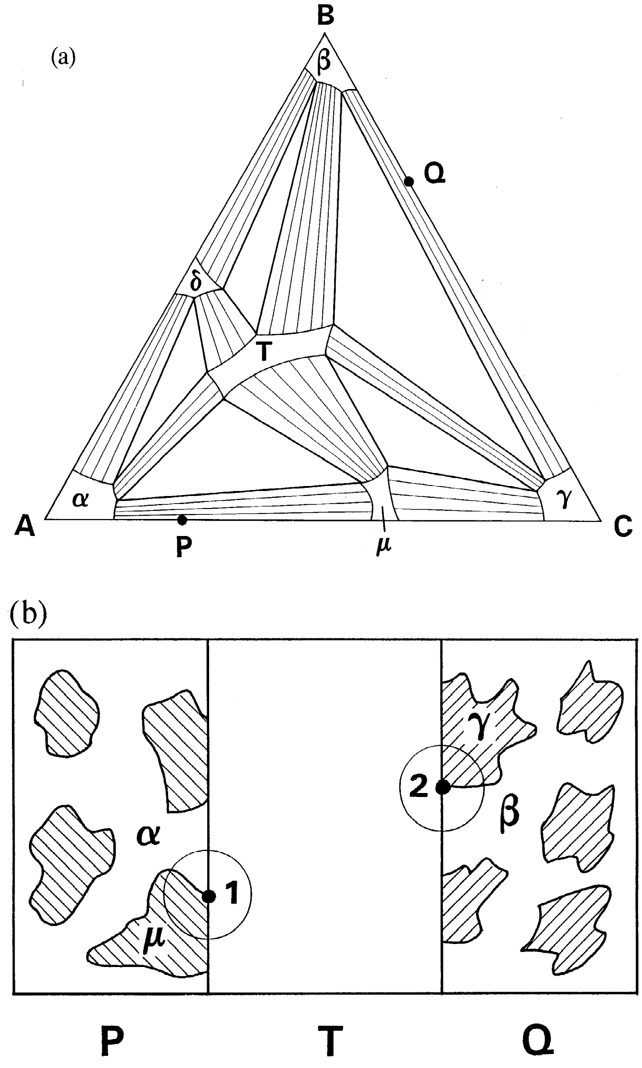


Fig. 2. Determination of the phase equilibria on the isotherm of the ternary A–B–C system using two-phase alloys as end-members (a) and schematic view of a possible reaction zone in a hypothetical diffusion couple P/Q (b).

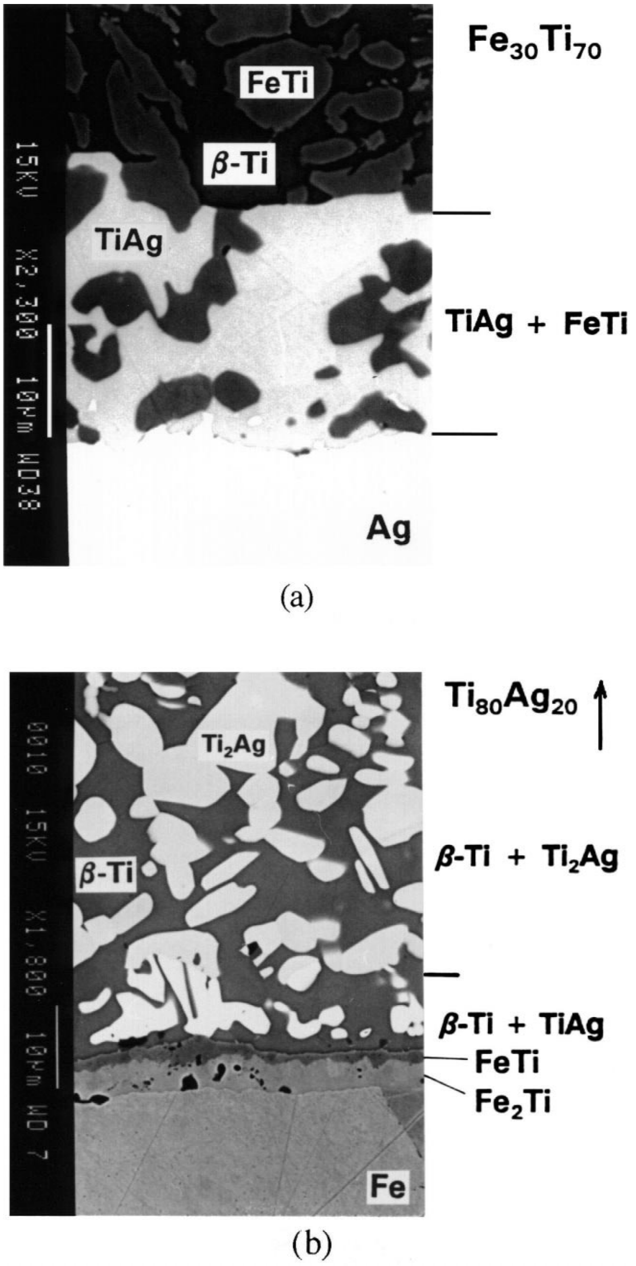


Fig. 3. Reaction zone morphologies developed after annealing (850°C; 100 h; vacuum) in the diffusion couples based on: (a) $Fe_{30}Ti_{70}$ two-phase alloy and Ag; (b) two-phase $Ti_{80}Ag_{20}$ alloy and Fe. Secondary and backscattered electron image, respectively. Note, in (b) the original (α-Ti + Ti_2Ag) alloy is much further away from the interface (about 500 μm).

formed. The β-Ti matrix is also a constituent of the next two-phase layer β-Ti + Ti_2Ag adjacent to the initial two-phase Ti–Ag alloy. (Note: silver stabilizes the hexagonal α-Ti structure, while the presence of Fe increases the stability of the bcc β-Ti-based solid solution [16].) The composition of the β-Ti-based solid solution in equilibrium with the intermetallic compounds Ti_2Ag and TiAg inside the diffusion zone was determined as $Ti_{84.0}Fe_{13.5}Ag_{2.5}$. Analysis of the morphology developed in this diffusion couple reveals the three-phase equilibria FeTi + TiAg + β-Ti, β-Ti + TiAg + Ti_2Ag and β-Ti + Ti_2Ag + α-Ti in the Ag–Fe–Ti system at 850°C. All equilibria found in the polyphase diffusion couples are consistent with the ternary Ag–Fe–Ti diagram given in Fig. 4. The experimentally established phase relations were also confirmed by examining a number of ternary equilibrated alloys and, in addition, they were verified by a thermodynamic evaluation of this system [15].

Further development of this technique for studying phase diagrams is connected with changing the ‘macrostructure’ of the classical diffusion couple. A sample is prepared by joining two plane-parallel slices of metal (alloy) through a thin layer of the third metal (alloy) as is shown schematically in Fig. 5a. In such a layered system,

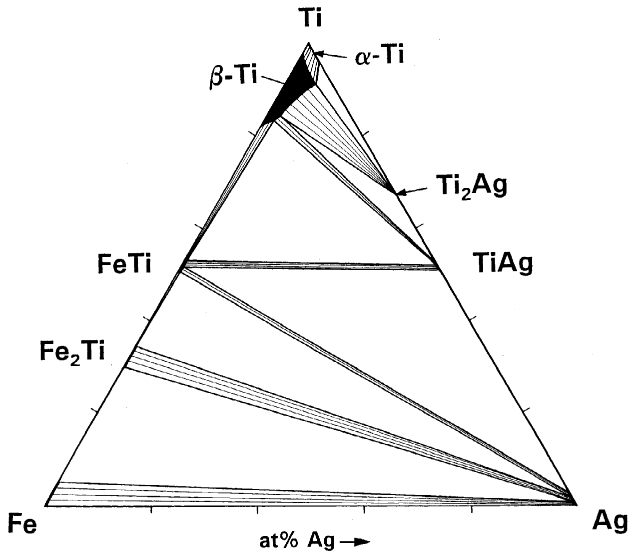


Fig. 4. Isothermal cross-section through the ternary phase diagram Ag–Fe–Ti at 850°C [15].

in which the central part is eventually consumed, the diffusion path is not fixed as in the semi-infinite couple. The phase composition of the complex diffusion zone is changing continuously with time as a result of the overlapping of two quasi-equilibrated diffusion zones. To relate the morphology and composition of the reaction zone to the phase diagram, rules similar to those explained before still can be used. For instance, in Fig. 5 the composition found in the phases α_1 and α_2 at $t = t_3$ and t_4, respectively, are the end points of two tie-lines in the two-phase region.

In order to elucidate this variant, let us consider a relatively simple example of constructing an isothermal section of the ternary Ni–Cr–V system at 1150°C. In this case, the basic idea of the technique was realized in the following way: the 'sandwich' samples were prepared by joining and subsequent annealing at 1150°C in vacuum of vanadium and chromium discs (about 2 mm thickness) with an intermediate Ni-foil. It is imperative that before the process of interference starts, local equilibria have been established inside the reaction zone in each of the 'semi-infinite' couples of which the 'sandwich' sample was originally composed. Based on the information about diffusion kinetics in the constituent Ni/V and Cr/Ni binary couples [17], the thickness of the Ni-interlayer was chosen as 100 μm.

Examination of the 'sandwich' samples after heat treatment at 1150°C for 4, 16 and 25 h revealed the formation

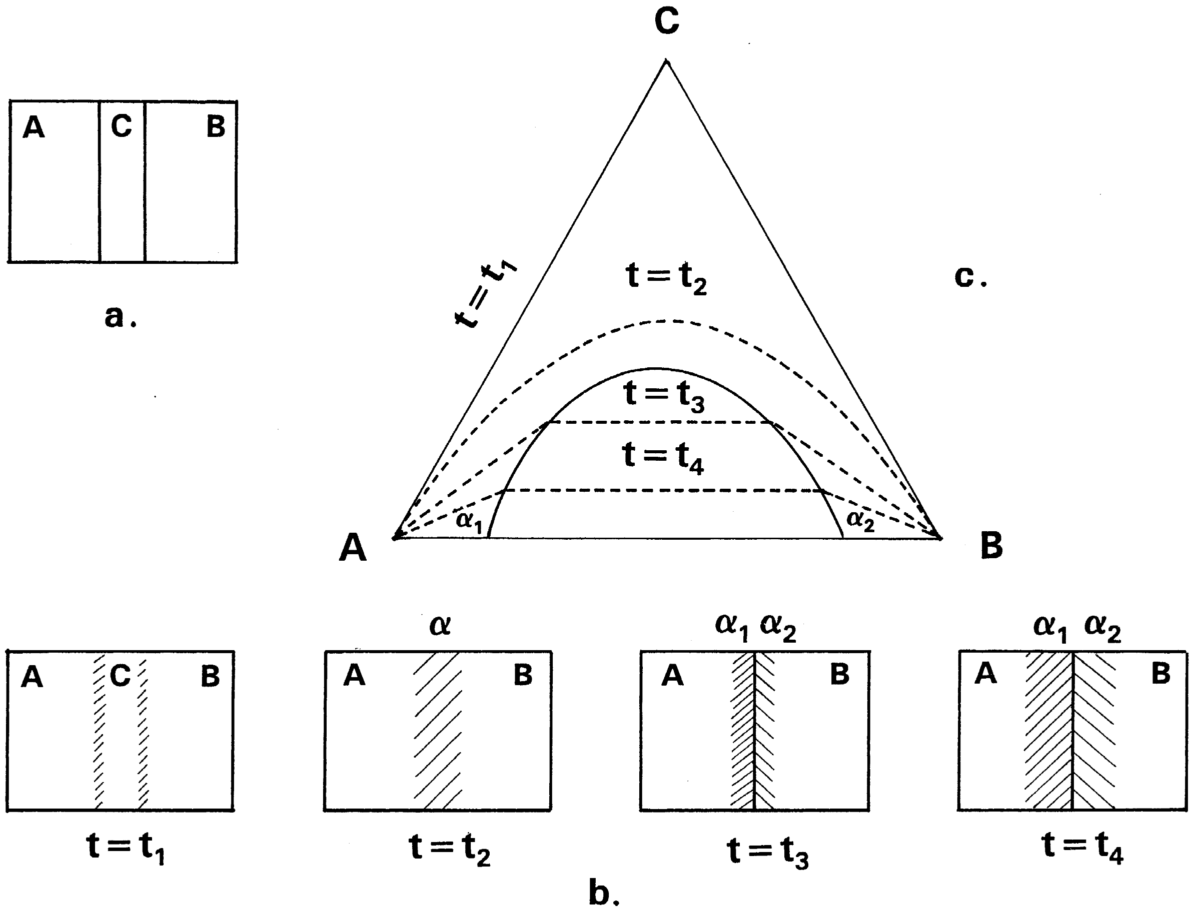
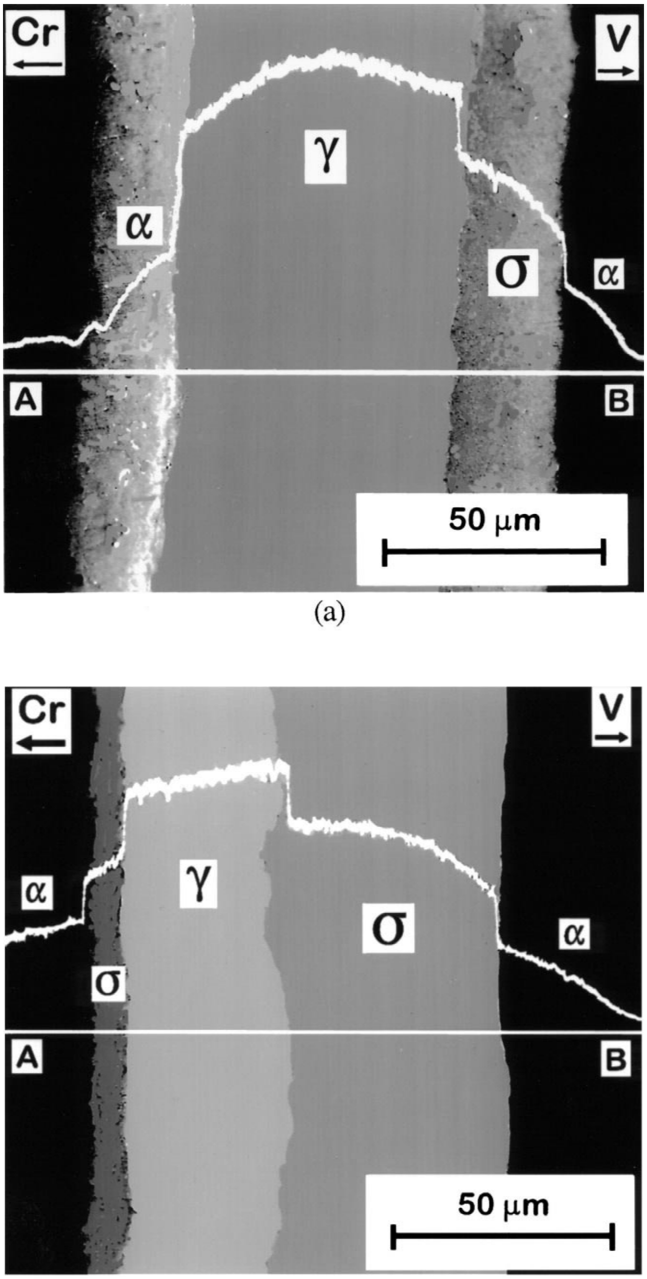


Fig. 5. Schematic view of the reaction zones and diffusion paths on an isotherm after various annealing times: (a) initial 'sandwich' sample; (b) reaction zone morphology for different annealing times; (c) diffusion paths for various annealing times.

at the vanadium-side of the diffusion zone a continuous layer of the σ-‘VNi’ phase containing some chromium. A typical microstructure of the reaction zone after the annealing is shown in Fig. 6a. The chromium content in the product layer was found to increase with increasing reaction time. The reaction layer growth obeys a parabolic law, thus, the process of layer formation is diffusion-controlled.



(a)

(b)

Fig. 6. Microstructure of the diffusion zone in the finite ‘sandwich’ sample V/Ni, foil (100 μm)/Cr after annealing at 1150°C in vacuum for: (a) 16 h and (b) 49 h. Backscattered electron images together with the variation in the Ni-Kα signal across the zone of interaction (along the line AB). The fcc and bcc solid solutions are denoted as γ and α, respectively.

Subsequent annealing of the sample up to 49 h led to the reaction zone morphology shown in Fig. 6b. A characteristic feature of the diffusion zone developed under these conditions is the formation of two layers of the σ-phase, separated by a layer of the Ni(V,Cr)-based solid solution. The latter observation indicates that the diffusion path crosses the σ-phase field on the ternary Ni–Cr–V isotherm twice.

This isotherm was also investigated using ‘semi-infinite’ couples of the NiCr/V type and by means of traditional methods of equilibrated alloys. Fig. 7 represents the experimentally determined isotherm and the diffusion paths found in the ‘sandwich’ samples after various annealing times. One can see that the results obtained by the different techniques are in good agreement.

Before ending this part of the discussion, it should be mentioned that within the past 12 years this variation of the diffusion couple technique has proven itself as a valuable tool in phase diagram studies (see, for example, Refs. [18–21]). The efficiency of this method is very high. By making only one finite ‘sandwich’ sample, re-annealing and investigating after various annealing times, a lot of information can be gained about the whole isotherm.

As demonstrated in the preceding sections, at an elementary level, the diffusion couple technique is nothing more than a tool for establishing a correlation between the morphology developed in the diffusion zone of the couple and a certain type of phase relations in the system. However, it must be added immediately that like in the case of other seemingly simple methods used in materials science, the proper use of diffusion couples for determination of multicomponent phase diagrams is by no means a trivial procedure as it might look at first sight. A number of

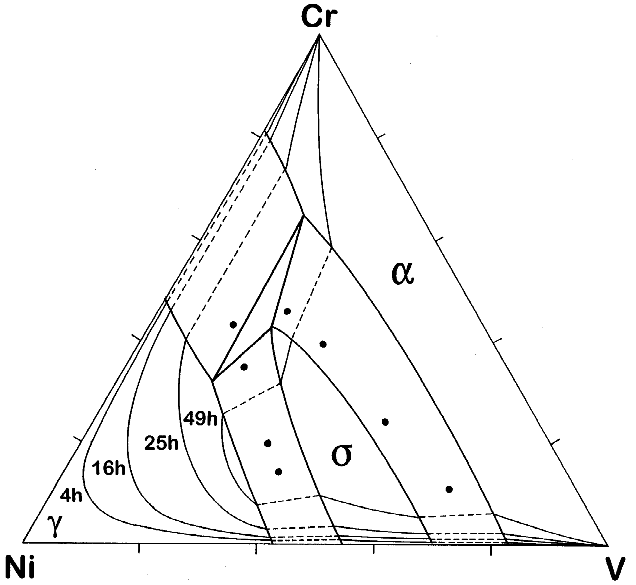


Fig. 7. Experimentally determined isothermal cross-section through the Ni–Cr–V phase diagram at 1150°C [17]. The compositions of the equilibrated alloys examined are depicted as points.

error sources may appear when multiphase diffusion experiments are used for establishing phase equilibria.

5. Error sources encountered in the diffusion couple technique

The experimental results may contain errors directly attributable to the nature of the sample. One of the possible dangers of technical importance is a system in which the terminal compositions (end-members) are solids, but a liquid phase exists at the annealing temperature. It is then possible for the diffusion path to wander into this field, with disastrous results indeed! Poor adherence at the interfaces in the diffusion zone and accelerated reaction rates due to defects such as cracks, grain boundaries, etc. may also render the interpretation of diffusion couple experiments cumbersome.

Another source of error is in the experimental measurements themselves. The difficulties connected with the accurate determination of the boundary concentrations in the reaction zone are a problem for both semi-infinite and finite diffusion couple techniques. Several items concerning the electron-beam microanalytical techniques used are to be noted here.

Firstly, the determination of a chemical composition with EPMA has an inherent experimental error associated with data counting statistics and data correction procedures.

Secondly, the volume of X-ray generation in the 'bulk' samples is determined by the electron scattering in the target, and not by the incident electron beam size. Because of the scattering effects, it is impossible to generate characteristic X-rays from (and hence, to determine the chemical composition of) a volume much smaller than 1–2 μm in diameter. In other words, explicit measurements of interfacial compositions are not possible with any electron-beam technique. It is, however, possible to measure concentration gradients in the vicinity of the interfaces in the multiphase diffusion zone. When the phases in question have a reasonable layer width, the composition at the interface can be determined by extrapolation of the measured concentration profile and to extract the actual concentration profile, and therefore the interface composition. This approach, however, is not always very accurate. In most cases, the necessity for extrapolation is the most serious limitation of the EPMA. Moreover, steep concentration gradients may occur near the phase boundaries in the diffusion-grown layers, and then, the extrapolation leads to even larger errors. The same problem arises, by the way, when the equilibrium compositions at precipitate/matrix interfaces in a two-phase reaction product are determined.

Thirdly, the X-ray absorption effect, which occurs when X-rays produced at one point within the specimen travel through materials of different compositions, and, perhaps, of different mass absorption coefficients on their way to the spectrometer. To avoid such absorption effects, it is necessary to orient the phase boundary in the diffusion couple perpendicular to the sample surface and the interphase interface parallel to the X-ray path to the spectrometer.

Finally, accurate microprobe analysis near the interfaces is sometimes very difficult owing to fluorescence effects. When dealing with the problem of spatial resolution in quantitative electron probe microanalysis, it is very often the range of electron propagation, people are primarily concerned about. The latter can be defined as the distance the electrons diffuse away from the point of impact of the incident electron beam on the specimen until they have lost so much energy as to be no longer capable of exciting primary characteristic X-ray radiation. As already mentioned, this range is typically of the order of 1–2 μm yielding a volume of primary excitation of ~2–4 μm diameter. In many cases, however, the primary characteristic X-ray radiation can be powerful enough to excite one or more other elements present in the sample, thus giving rise to enhanced X-ray production i.e. fluorescence. In other words, if the sample contains a species of atoms with a critical excitation energy less then the energy of the primary characteristic X-rays being absorbed, fluorescence will occur. The main trouble here is that this 'characteristic' fluorescence usually takes place in a much larger volume. The latter can be an order of magnitude greater than the volume of primary excitation due to the fact that X-rays can travel much more easily through matter than electrons can. As a consequence, the spatial resolution can be drastically lowered. In fact, in analyzing multiphase couples the additional X-ray excitation may occur on one side of the phase interface even though the electron beam and the analysis point is on the other side of the interphase interface. This may lead to the peculiar observation that X-rays of a certain element may be detected in locations where the element is not present. In this context, it is relevant to mention that for the case of K–K fluorescence (Kα-radiation of one element exciting Kα-radiation of the other), the excitation of secondary radiation is especially bad in targets containing elements with atomic numbers differing by two (for atomic number $Z>21$), like combinations of the elements Fe/Ni, Cu/Co, etc.

In general, in order to avoid the problem of fluorescence (and absorption) 'uncertainty', a number of correction schemes have been introduced [10]. One should, however, keep in mind that in all these correction procedures it is implicitly assumed that the primary and secondary production of X-ray radiation as well as subsequent absorption all take place in the same homogeneous (single phased) matrix. Apparently, these conditions are violated to increasing extent as the incident electron beam approaches an interface or when the size of particles decreases below a certain limit. Corrections for this effect are possible but difficult [22]. It is best to determine how large the effect is by using undiffused couples and to correct the data accordingly. In a binary diffusion couple, usually one of the elements does not suffer from the fluorescence effect and one could measure the concentration of that element by microprobe analysis to describe the distribution of elements across the reaction zone. If, for instance, pure Cu and Co are clamped together, without any diffusion taking place, Co Kα characteristic X-ray radiation can apparently be measured at a distance of up to 40 μm from the interface in the pure Cu [22]. About 4.8 at.% of Co appears to be in Cu at the interface. Measuring Co Kα radiation diminishes the error, but still an apparent concentration of 2 at.% is found in cobalt near the interface, whereas the Cu X-ray radiation can be detected at about 15 μm from the interface in cobalt.

Obviously, in the case of a ternary system, the situation can be even more intricate. Space being limited, the reader interested in greater detail concerning the correction procedures is invited to turn his attention to the references cited.

Another group of problems arise from the formation of a quasi-equilibrated diffusion zone. When the diffusion couple techniques are used for phase diagram determination, it is of fundamental importance to be sure that equilibrium values are 'really' attained at the interphase interfaces and that all equilibrium phases pertaining to the system under the conditions of the diffusion couple experiment, are formed in the reaction zone.

Sometimes certain phases seem to be missing in a diffusion couple when investigated by microscopic or microprobe analysis. One of the reasons for the absence of an equilibrium phase might be the presence of a barrier layer at the interface, such as, for example, oxide films at the contact surface or the presence of impurities in the starting materials. In the latter case, the segregation of impurities, which may be present only in the ppm-range in one of the end-members can cause enrichment in the diffusion zone, making nucleation of a certain phase difficult.

Even though the absence of certain phases might be due primarily to difficulties in nucleation, it is important to point out that the apparent absence of a particular intermediate phase in a diffusion zone cannot automatically be interpreted as the result of nucleation problems. It is possible that the phase is present in such a minute quantity that it cannot be determined easily by the experimental techniques available. It should be noted that a kinetic consideration of product phase growth in itself is not so essential for the present discussion. However, when taken in the overall context of a diffusion couple experiment, the question of the apparent absence of a certain equilibrium phase in a reaction zone or, conversely, the formation of metastable phases during interaction, becomes an important issue. For instance, in a 'notorious' example of a Ti/Al diffusion couple only $TiAl_3$ was found [23]. Yet, several other intermetallic phases should have been formed according to the phase diagram [16]. On the other hand, when incremental $Ti/TiAl_3$ diffusion couples were annealed at 800°C, all the possible intermetallic phases according to the equilibrium phase diagram, were indeed found in the reaction zone: $Ti/Ti_3Al/TiAl/TiAl_2/TiAl_3$. However, when a layer of Al was joined on the outside of the $TiAl_3$ layer of the above couple and annealed at 625°C for 15 h, the compounds $TiAl_3$, TiAl and $TiAl_2$ disappeared, resulting in the basic original configuration of $Ti/TiAl_3/Al$. Clearly, in this case nucleation of Ti_3Al, TiAl, $TiAl_2$ cannot be the problem. Rather, the apparent absence of the other phases is due to the relatively slow diffusion in these compounds, i.e. due to slow growth kinetics.

An additional reason for caution here is that occasionally a non-equilibrium phase, often stabilized by impurities present in terminal materials, can grow in a diffusion zone. Very telling examples of such a situation are carbides like Mo_5Si_3C [24] or Mo_6Ni_6C [25], which might be confused with the purely binary phases Mo_5Si_3 and MoNi. The same is true for oxides, e.g. Ti_4Ni_2O and nitrides like Nb_4Ni_2N, which might be confused with the binary compound Ti_2Ni or with an, in fact non-existing, binary 'compound' Nb_2Ni. Further complications may result from the fact that the 'impurity stabilized' phases often grow in series with genuine binary compound layers, like it is shown in Fig. 8 for the Nb/Ni couple annealed at 1100°C. Three distinct product layers are clearly visible on the micrograph. According to the binary Nb–Ni phase diagram, however, only two products are expected to form in the reaction zone of the Nb/Ni couple at this temperature:

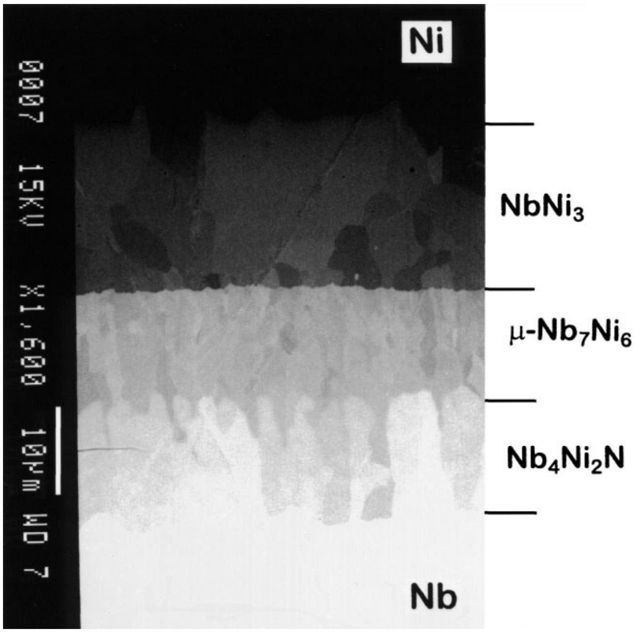


Fig. 8. Backscattered electron image of an annealed (1100°C; 196 h; vacuum) binary Nb/Ni couple showing the formation of the 'impurity stabilized' phase Nb_4Ni_2N within the reaction zone.

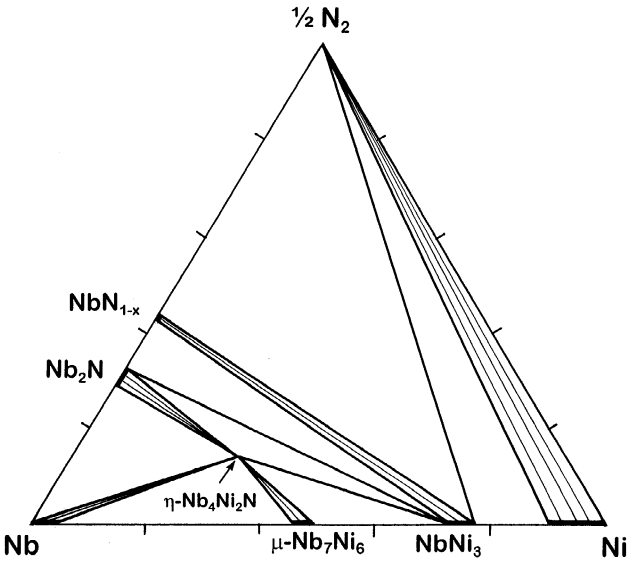


Fig. 9. The ternary Nb–Ni–N phase diagram at 1100°C and 10^{-8} bar of nitrogen partial pressure [26].

$NbNi_3$ and the μ-phase Nb_7Ni_6 [16]. Electron probe microanalysis revealed that the reaction layer formed at the Nb-side of the diffusion zone is a ternary compound with a composition close to the Nb_4Ni_2N, which indeed exists in the ternary Ni–Nb–N system at 1100°C (Fig. 9) [26].

An easy way to verify the purely binary character of an equilibrium phase layer is the use of incremental couples. The terminal compositions are then chosen quite close to the apparent phase in question, in such a way that only this phase might be formed. The end-members may be single-phase or two-phase alloys. A true equilibrium phase then grows parabolically with time as a relatively thick layer, whereas an impurity-stabilized phase ceases to grow after some time since the impurity from the end-member is totally consumed [27].

6. Concluding remarks

Unquestionably, the diffusion couple technique is a powerful and viable technique in establishing phase relationships. The efficiency of this method is very high. Yet, it is not without its shortcomings. One area which has room for improvement is in spatial resolution of the microanalytical techniques used. Errors attributable to extrapolated interface compositions can then be minimized and steeper concentration gradients can be measured. In this respect, analytical electron microscopy (AEM) has a promising future. However, problems of specimen contamination, X-ray absorption and quantification procedures as well as preparation of reproducible thin-film samples in the AEM have yet to be solved.

It should be also stated that although the diffusion couple technique is a unique and powerful tool in materials science studies, it is especially useful in conjunction with other methods. For instance, in order to increase the reliability of the information obtained about a ternary isotherm, a combination of the diffusion methods with an investigation of selected equilibrated alloys is desirable. Multiphase diffusion couples can be used to map out a constitutional diagram and select the compositions of the alloys to be examined. The precise location of the phase field boundaries can be obtained from equilibrated samples.

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