SPECIAL SECTION IN HONOR OF ROBERT W. CAHN

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Reliability of the diffusion-multiple approach for phase diagram mapping

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The diffusion-multiple approach can be used to map phase diagrams at an efficiency orders of magnitude faster than the conventional equilibrated alloy method. This paper addresses a concern about the reliability of the results, especially whether the data obtained from diffusion multiples can produce reliable equilibrium phase diagrams. The following topics will be discussed: (a) establishment of local equilibrium at the phase interfaces, (b) X-ray interaction volume vs. thickness of the phases (microprobe related issues), (c) reliability of phase diagrams from equilibrated alloys, (d) usefulness of electron backscatter diffraction, (e) impurity-induced stabilization of metastable phases, and, (f) missing phase situations. A direct comparison of several ternary systems obtained from both diffusion multiples and equilibrated alloys was made. The good agreement between them clearly demonstrates the reliability of phase diagrams determined from diffusion multiples.

1. Introduction

The first graphical representation of phase equilibria, what we now call a phase diagram, was that of Roberts in 1875 on the Cu-Ag system [1]. Some 4700 diagrams have since been documented out of a set of ∼4950 binary systems, but only ∼15,000 diagrams of a total possible 161,700 ternary systems [2]. John Elliot stressed that phase diagrams are maps for metallurgists and therefore indispensable for both research and application. While binary diagrams are relatively simple to determine experimentally, the legendary William Hume-Rothery once said that it took a master's degree student to determine one isothermal section of a ternary phase diagram. The slow and laborious work involved in determining phase diagrams makes these extremely useful maps often unavailable to materials scientists who would use them to guide up-front design of materials. Robert Cahn himself did not make phase diagram determination a major part of his research, although he has made some contributions both to phase diagrams (e.g. [3, 4]) and to techniques for their determination [5, 6]. Cahn in the year 2000 stated that "I expect to see this [high-efficiency] approach developed in the near future; then the years involved in determining a ternary phase diagram will be drastically shortened . . . " [7]. Cahn's prediction was correct. A year later, a diffusion-multiple approach was developed for rapid mapping of phase diagrams and phase properties [8, 9]. At about the same time, the continuous phase diagramming (CPD) approach based on thin film deposition was also developed for rapid mapping of phase diagrams [10]. This article will only discuss the diffusion-multiple approach and readers are referred to the work of Yoo *et al.* for the CPD approach [10]. The diffusion-multiple methodology can be orders of magnitude more time-efficient than the traditional equilibrated alloy method in phase diagram mapping. This paper will address two related concerns: (1) how reliable are the phase diagrams determined from diffusion multiples? and (2) are they real equilibrium phase diagrams?

2. The diffusion-multiple approach

A diffusion multiple is an assembly of three or more different metal blocks, in intimate interfacial contact, and subjected to a high temperature to allow thermal interdiffusion [8, 9, 11]. The interdiffusion among the elements forms all the intermetallic compounds and solid-solution phases in that ternary system, creating complete libraries of the single-phase compositions. The composition libraries coupled with advanced micro-analytical techniques such as electron probe microanalysis (EPMA), electron backscatter diffraction (EBSD) and nano-indentation make diffusion multiples a powerful approach for structural materials research and development. This paper will only address the phase diagram mapping part of the diffusion-multiple approach.

A diffusion-multiple example is shown in Fig. 1 [12]. It was made by cutting a slot of 1.8 mm width and 12.7 mm length from a 25 mm diameter pure Cr disk of 3 mm thickness. Pure Pd, Pt, and Rh foils of 0.25 mm thickness are arranged in a bricklaying geometry shown in Fig. 1b and put into the slot in the Cr disk along with a pure Ru piece with 2 steps on it. The Ru piece had a thickness of 1 mm on one side and 0.5 mm on the other. Two pure Cr disks (without the slot) of 25 mm diameter and 3 mm thickness were placed on top and

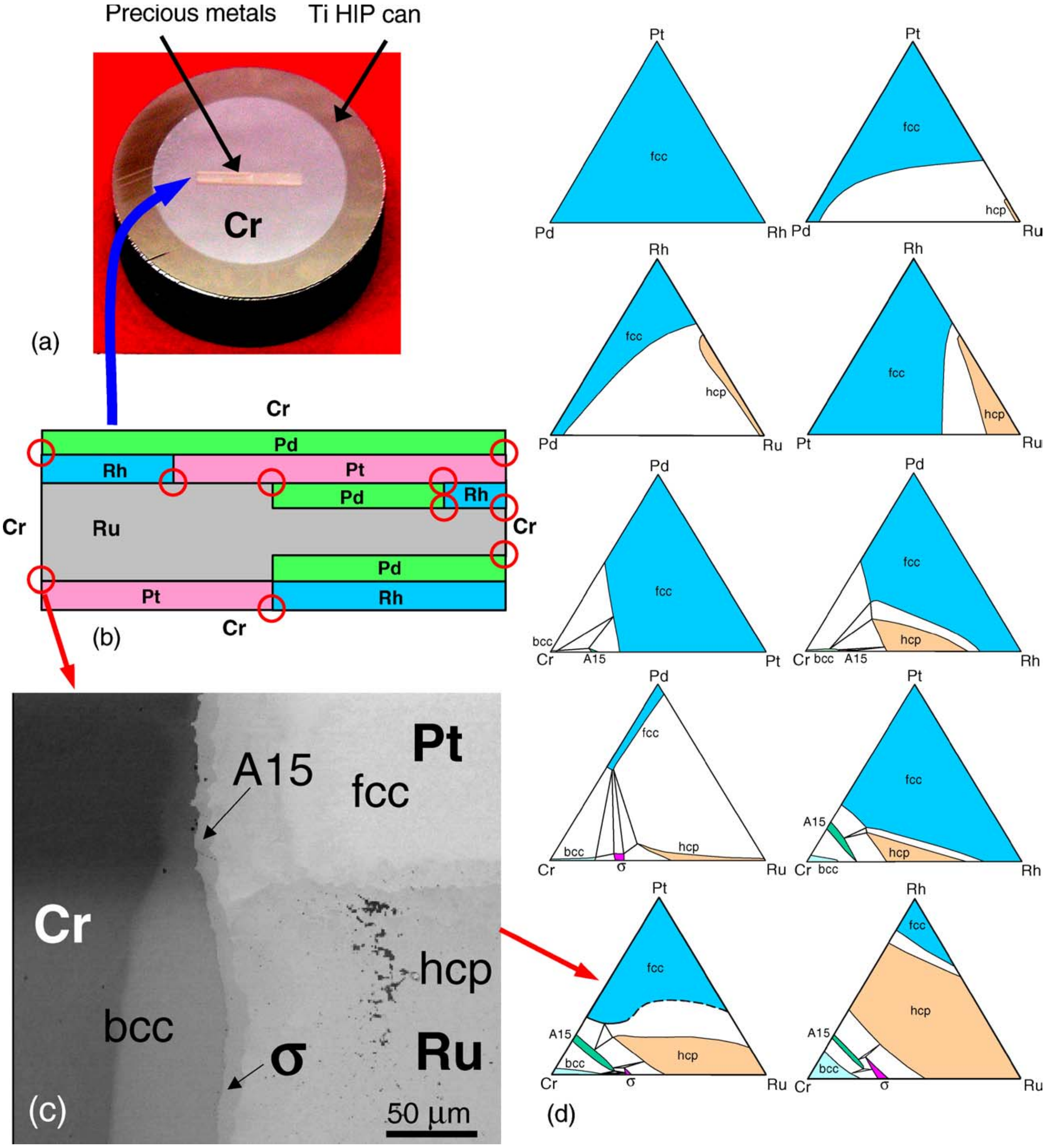


Figure 1 A diffusion multiple for rapid mapping of ternary phase diagrams in the Pd-Pt-Rh-Ru-Cr system [12]: (a) an optical image of the sample (see text for the exact size); (b) the arrangement of the precious metal foils in the diffusion multiple to create many tri-junctions shown in circles; (c) a backscatter electron image of the Cr-Pt-Ru tri-junction showing the formation of the A15 and σ phases due to interdiffusion of Pt, Ru and Cr; and (d) ten ternary phase diagrams (isothermal sections at 1200°C) obtained from this single diffusion multiple. The phase diagrams are plotted in atomic percent axes with the scales removed for simplicity.

bottom of the slotted Cr disk containing all the precious metals. The assembly was then placed in a pure Ti tube of 25.5 mm inner diameter and 32 mm outer diameter and 9.6 mm height. Two Ti disks of 32 mm diameter and 3 mm thickness were placed on the top and the bottom of the Ti tube filled with the three Cr disks. The assembly was evacuated and then welded in vacuum using an electron beam along the top and bottom peripheries of the Ti tube. The welded outer Ti tube and caps served as a hot isostatic pressing (HIP) can. The whole assembly then underwent a HIP run of 1200°C, 200 MPa for 4 h to achieve intimate interfacial contact among all these pieces. The diffusion multiple was further annealed at 1200°C for 36 h in a vacuum furnace—making the total diffusion exposure time 40 h at 1200°C. The Cr disks and the Ti HIP can serve as protection for the precious metals from any interstitial contamination during heat treatment. The diffusion time was chosen to develop diffusion profiles measurable over lengths of ∼100 microns, so that neighboring diffusion sources would not interfere with the couple or triple being evaluated.

The annealed diffusion multiple was then cut into halves parallel to the two Ti caps and at the mid-point

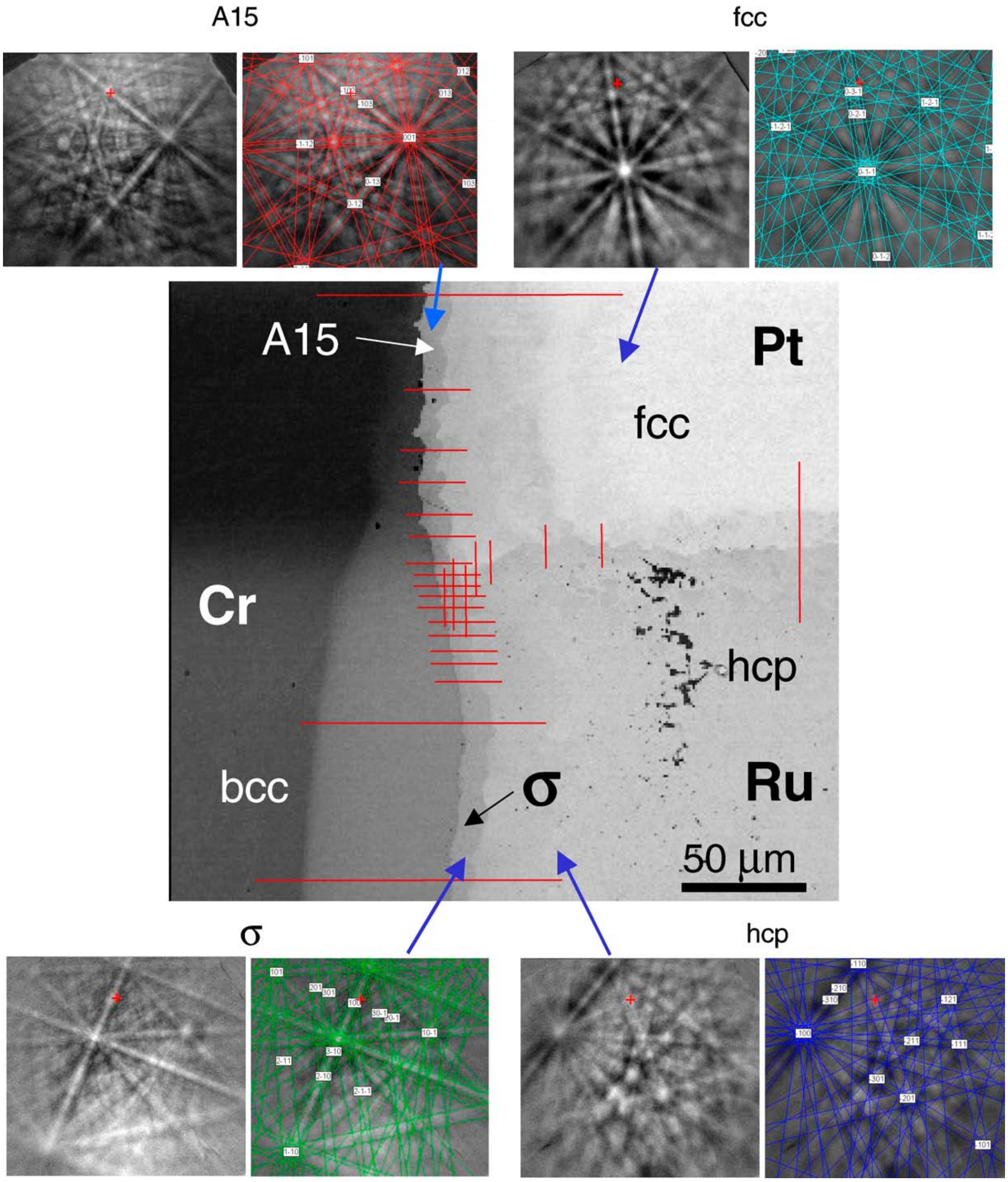


Figure 2 EBSD identification of phases in the Cr-Pt-Ru ternary system in the diffusion multiple. The lines on the SEM backscatter electron image (in the middle) represent the locations of the EPMA scans. The EBSD patterns are shown in pairs with the un-indexed pattern on the left and the indexed pattern on the right.

of the thickness direction (Fig. 1a). The sample was ground and polished for EPMA and EBSD evaluation. The bricklaying pattern allows the formation of ten tri-junctions in this diffusion multiple, as shown in Fig. 1b by the highlighted circles. Each tri-junction created a complete library of the single-phase compositions of that ternary system. A scanning electron microscopy (SEM) backscatter electron image (BSE) of the Cr-Pt-Ru tri-junction is shown in Figs 1c and 2. Based on the binary phase diagrams, there should be one intermetallic compound (Cr_3Pt with an A15 crystal structure) formed between Cr and Pt, and also one compound (σ with a tetragonal crystal structure) between Cr and Ru. There should be no compound between Pt and Ru, just the fcc/hcp equilibrium. The image in Figs 1c and 2 clearly shows the A15 (Cr_3Pt) and the σ phase and a clear fcc/hcp phase boundary. It is difficult to locate the phase boundary between the A15 and the σ phase using the SEM BSE image alone; however, the EBSD technique was very useful in helping to identify the phase boundaries.

EPMA scans were performed along the line locations shown in the middle of Fig. 2. The composition profile of a representative EPMA scan is shown in Fig. 3a. Local equilibrium at phase interfaces allows accurate evaluation of equilibrium tie-lines. This will be discussed in more detail subsequently. By taking advantage of the local equilibrium at the phase interfaces, the tie-line

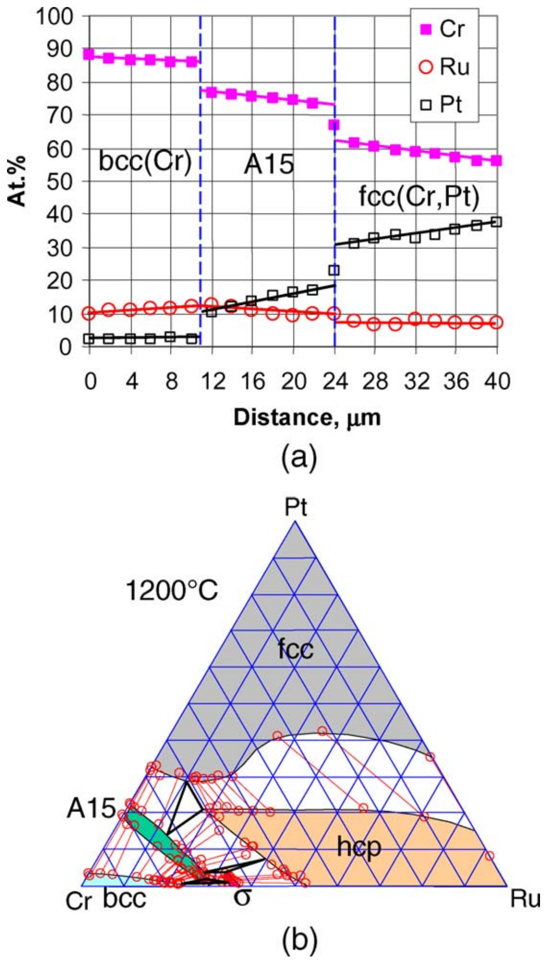


Figure 3 EPMA analysis of the Cr-Pt-Ru ternary system from line scans shown in Fig. 2: (a) a line scan showing a typical composition profile as produced by EPMA and (b) all the tie-line information based on the EPMA scans for the construction of the Cr-Pt-Ru ternary phase diagram.

compositions were evaluated by extrapolating the concentration profiles to the phase interfaces as shown in Fig. 3a. Based on the tie-line compositions obtained from all the EPMA scans shown in the middle of Fig. 2, the entire isothermal section of the Cr-Rh-Ru ternary system was obtained (Fig. 3b). By performing similar analysis on all the ternary junctions shown in Fig. 1b in circles, a total of 10 ternary phase diagrams were mapped from this single diffusion-multiple sample—it would probably take more than a thousand alloys to map these diagrams using conventional techniques. Thus, there is an orders-of-magnitude increase in efficiency compared to the individual alloy method.

Since none of the ten phase diagrams were available in the literature for comparison of the results from the diffusion multiple with those from equilibrated alloys, a comparison of several other systems where literature data are available will be made as a direct check for the reliability of the results from diffusion multiples.

3. Comparison of phase diagrams obtained from diffusion-multiples with those from equilibrated alloys

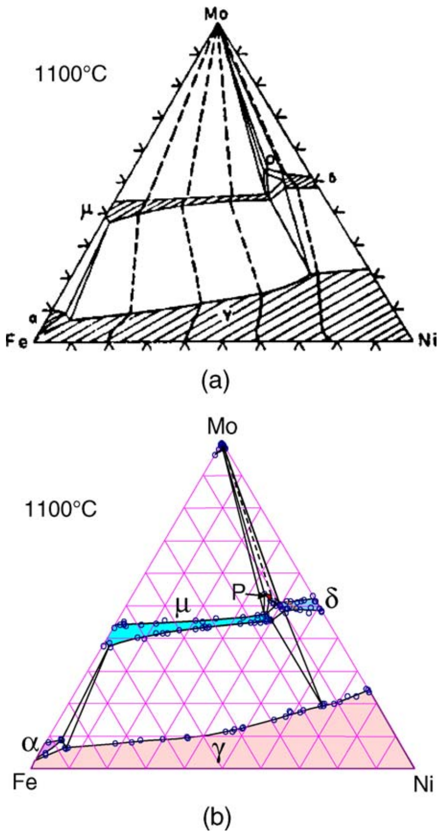


Figure 4 Comparison of the 1100°C isothermal section of the Fe-Mo-Ni ternary system: (a) results obtained from 23 equilibrated alloys and 7 diffusion couples [13] and (b) results obtained from a diffusion multiple [9].

A direct comparison of the 1100°C isothermal sections of the Fe-Mo-Ni and Co-Mo-Ni ternary systems is made in Figs 4 and 5, respectively [9, 13, 14]. Excellent agreement can be clearly seen. The literature data were based on results from both equilibrated alloys and diffusion couples from van Loo and co-workers [13].

Excellent agreement was also observed in the 1000°C isothermal section of the Ti-Cr-Al system, Fig. 6 [15, 16]. The isothermal section shown in Fig. 6a was constructed by Shao and Tsakiropoulos [15] based on results from more than a hundred alloys from several research groups. It can be seen by comparing Fig. 6 with Figs 4 and 5 that the number of alloys necessarily employed to determine a phase diagram rapidly increases as it becomes more complex. The advantage of the diffusion-multiple approach becomes more pronounced. Note that there is a slight difference in the solubility of Al in the bcc Cr phase. In addition, Shao and Tsakiropoulos did not separate the C36-Laves and the C14-Laves phases.

A direct comparison is also made for the 1200°C isothermal sections of the Nb-Ti-Al ternary system determined from equilibrated alloys and from a diffusion multiple, Fig. 7 [17–21]. Good general agreement is observed for the overall phase equilibria in the isothermal sections. However, difference can be seen, especially in the following areas: the α-Ti + $\beta+\gamma$-TiAl three-phase region, the σ phase composition in the $\beta+\delta+\sigma$ three-phase region, the width of the γ-TiAl single-phase region, etc. Even though the first four isothermal sections (Fig. 7a to d) were all determined from individual alloys, appreciable difference can be seen among them. Some of the difference may be related to the different

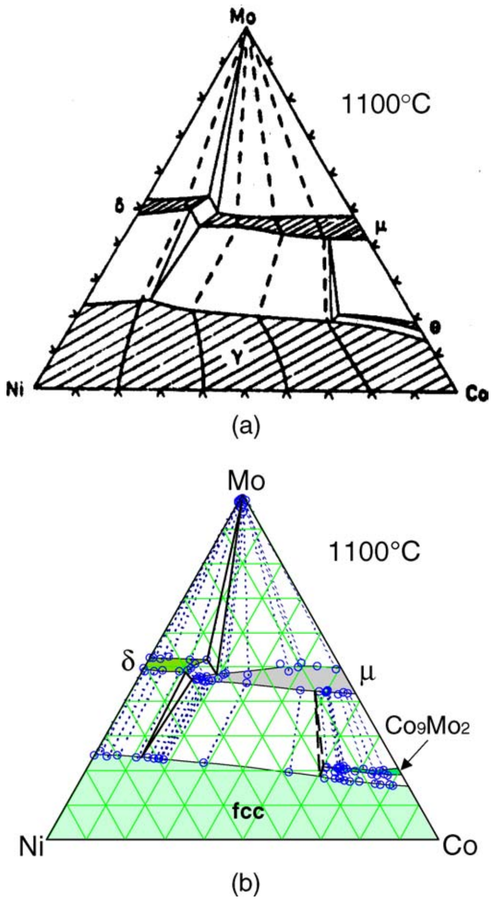


Figure 5 Comparison of the 1100°C isothermal section of the Co-Mo-Ni ternary system: (a) results obtained from 9 equilibrated alloys and 8 diffusion couples [13] and (b) results obtained from a diffusion multiple [14].

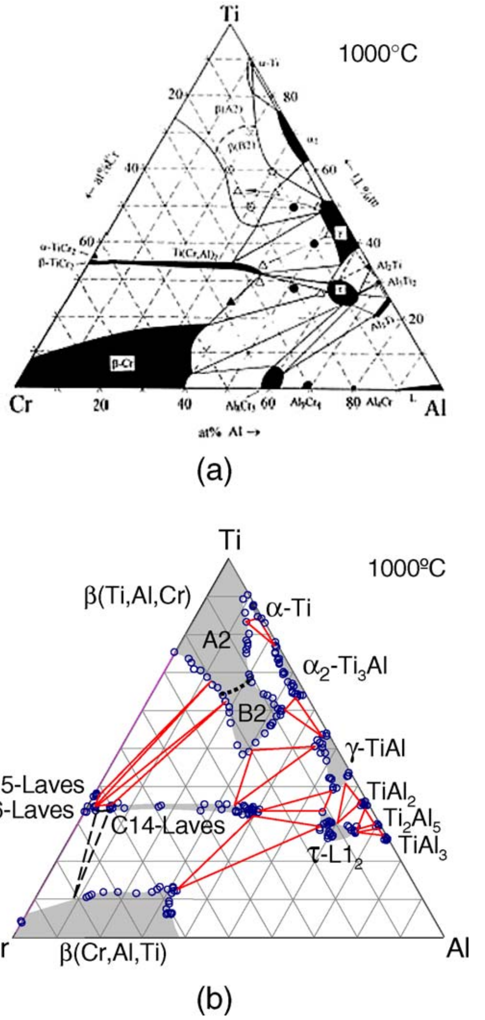


Figure 6 Comparison of the 1000°C isothermal section of the Ti-Cr-Al ternary system: (a) results based on more than 100 equilibrated alloys [15] and (b) results obtained from a diffusion multiple [16].

levels of interstitials (C, N, and O) in the alloys in this particular system.

The good agreement observed for these four ternary systems clearly shows that the phase diagrams obtained from diffusion multiples are reliable. Two additional systems will be discussed subsequently where significant disagreement is observed. It is argued that in both instances the phase diagrams obtained from diffusion multiples are more reliable than those obtained from individual alloys.

4. Discussion

4.1. Establishment of local equilibrium at phase interfaces

The existence and establishment of the local equilibrium at phase interfaces in diffusion couples have been demonstrated by many experiments over the past several decades. Excellent reviews on the topic were written by van Loo and co-workers [22, 23]. The establishment of local equilibrium at phase interfaces in diffusion multiples is not any different from that in diffusion couples. Local equilibrium at the phase interfaces is the basis for applying diffusion couples and also diffusion multiples to phase diagram determination.

It is worthwhile noting that the local equilibrium is only reached at the phase *interface*, not in the entire diffusion zone. Away from the interface, each infinitely thin layer of such a diffusion zone is *not* in thermodynamic equilibrium with the neighboring layers—the chemical potential (activity) gradient still exists at neighboring layers and will continue to drive diffusion if the sample is annealed for longer time. Only at the interface has the local equilibrium been maintained, and which serves as the base of applying diffusion couple/multiple techniques for determining equilibrium phase diagrams.

Deviations from local equilibrium are only likely to occur when the interface is moving at a speed in excess of D/a where D is the slowest diffusion coefficient and a is the atomic spacing. Such deviations may occur early in the heat treatment process, but are not likely after long-term annealing when the interface slows down.

Since the grain size of the phases is usually very large after a long-term diffusion anneal, the existence of coherent equilibrium at the interfaces is not very likely. The phase diagrams obtained from diffusion multiples should thus be equilibrium, non-coherent phase equilibria.

4.2. X-ray generation volume vs. thickness of the phases (microprobe related issues)

Measuring compositions across an interface is usually done using EPMA, with the inherent limitations of the

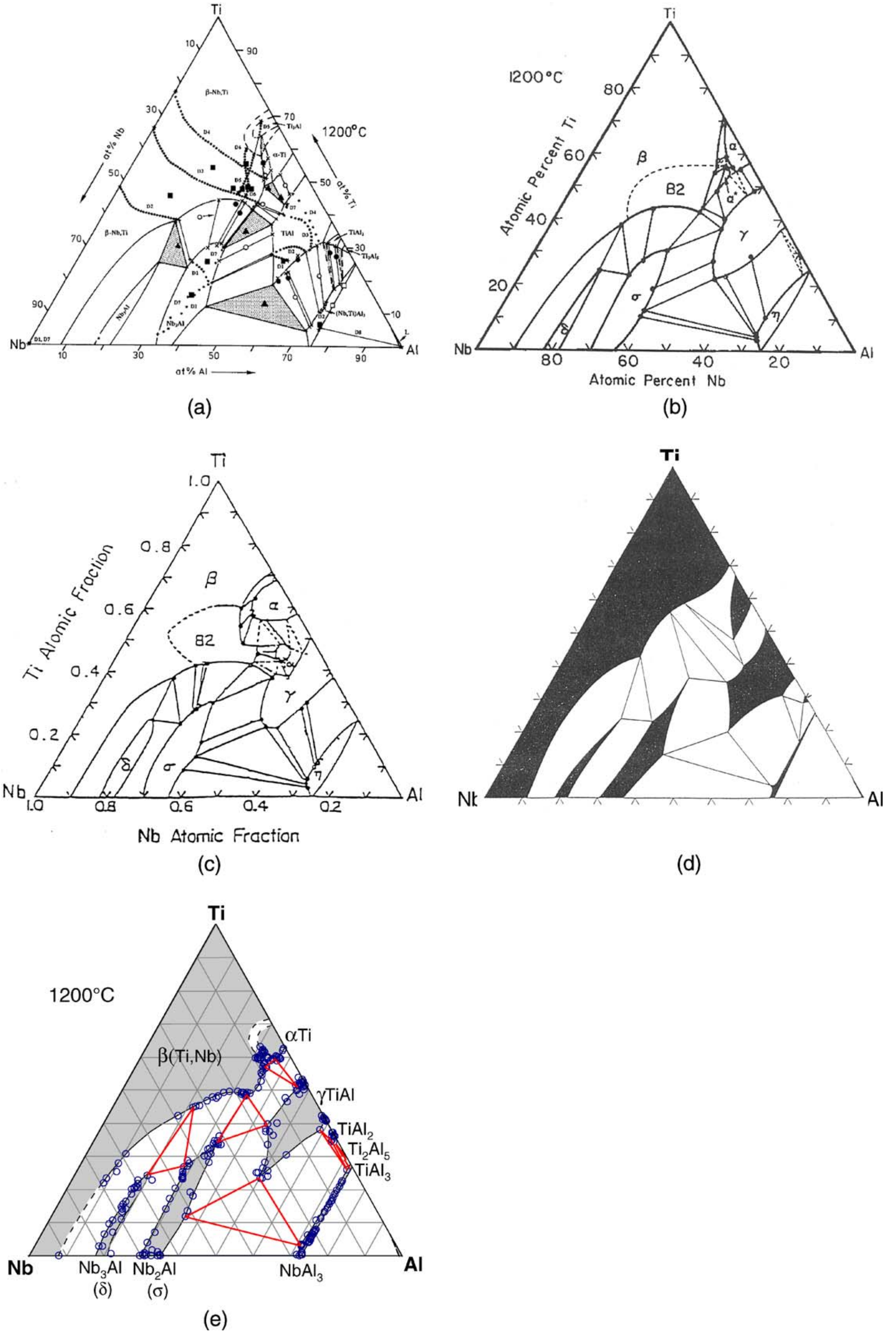


Figure 7 Comparison of the 1200°C isothermal section of the Nb-Ti-Al ternary system: (a) from Hellwig *et al.* [17] based on >70 alloys, (b) from Das *et al.* [18], (c) from Perepezko *et al.* [19], (d) from Kaltenbach *et al.* [20], and (e) from a diffusion multiple [21]. It can be seen that appreciable discrepancies exist in the reported phase diagrams, even between those (a) to (d) as well as in comparison with the diffusion multiple approach (e).

EPMA measurement volume in a homogeneous material being further degraded by measurement in a composition gradient. Since some phase layers formed in diffusion multiples are very thin (some of them are only a few microns in width), the questions are whether reliable phase compositions can be obtained by EPMA and whether extrapolation to the phase interfaces will produce reliable enough equilibrium tie-lines.

Monte Carlo simulations of the X-ray generation volume are performed to address the first question [24]. The volume from which X-rays are generated that reach the detector varies with atomic number of each

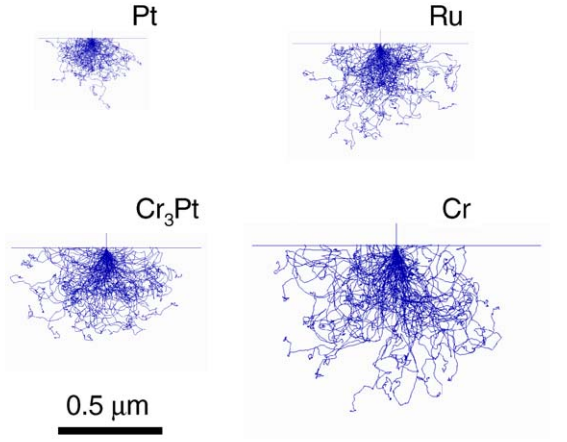


Figure 8 Monte Carlo simulation of the X-ray generation volume of four phases in the Cr-Pt-Ru ternary system. The simulation was conducted for an accelerating voltage of 15 keV with the electron beam at an 90° incident angle (perpendicular to the sample) [24].

constituent element. Some examples of such simulations are shown in Fig. 8 which provides critical information regarding the necessary thickness of the intermetallic compounds in the diffusion multiples and the "step size" for EPMA analysis. For instance, the X-ray excitation volume would be less than 1 μm^3 for the Cr_3Pt (A15) phase (Fig. 8); thus theoretically the thickness of this phase only needs to be a few microns to allow reliable analysis of its composition. The thickness of the Cr_3Pt phase in the precious metal diffusion multiple is only about 10 μm (Fig. 2), but it is more than enough to allow reliable EPMA analysis of several points using a 1-μm EPMA step, as shown in Fig. 3a. In addition, since the thickness is small and the interaction volume is also small, it makes sense to use a 1-μm step size for the analysis of the Cr-Pt-Ru region of the diffusion multiple.

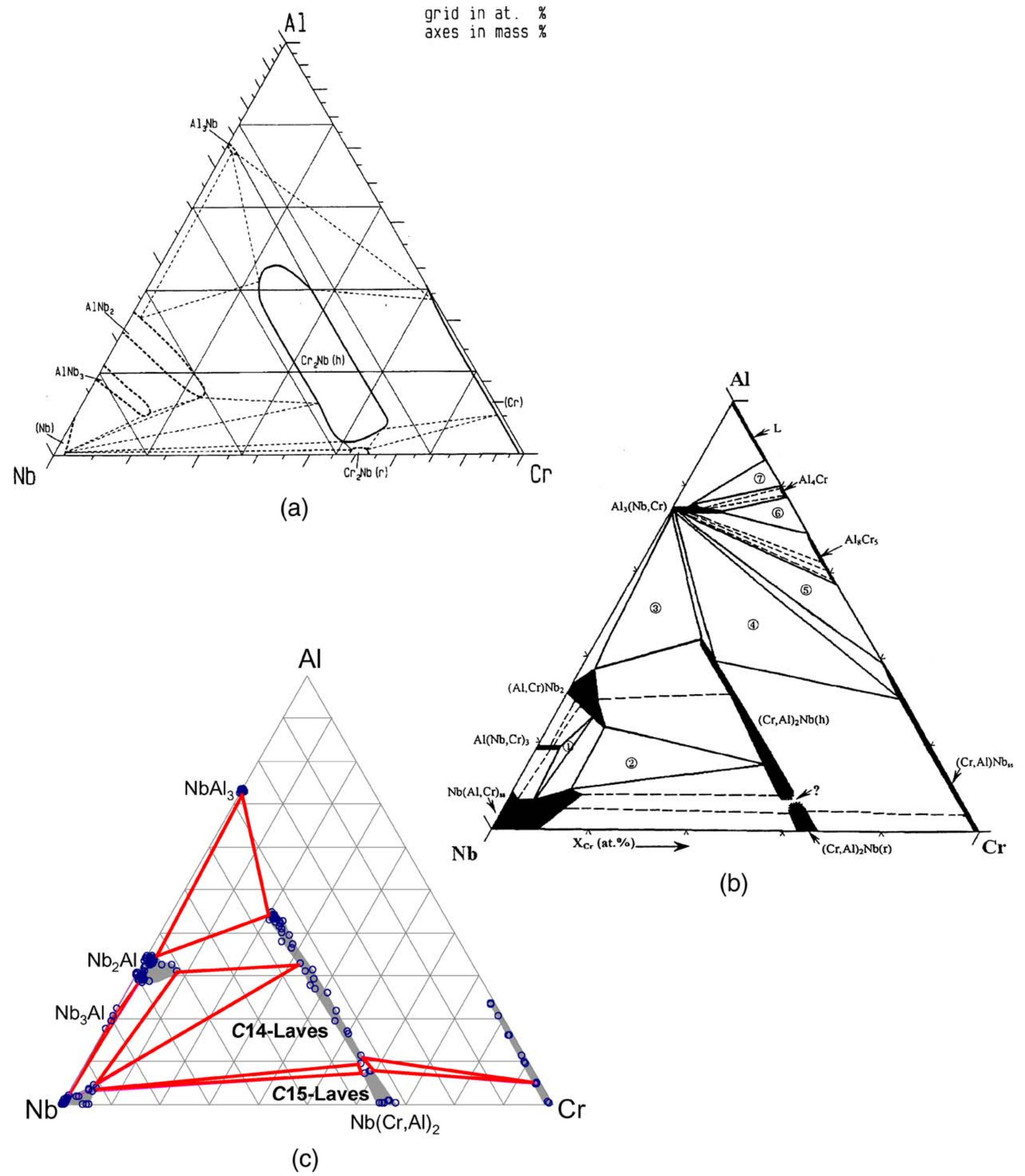
The Monte Carlo simulations also help the selection of the accelerating voltage used for the EPMA measurements. Low accelerating voltage is desired to reduce the X-ray interaction volume, thus allowing more reliable EPMA points to be obtained from thin phase layers. On the other hand, a higher voltage is desired for higher X-ray intensity and better peak-to-background ratios for higher efficiency EPMA data collection. An efficiency vs. accuracy trade-off analysis has to be made on a system-by-system basis to optimize the accelerating voltage and beam current. In the case shown in Figs 1 to 3, the accelerating voltage was selected to be 15 keV.

The reliability of compositional extrapolation to phase interfaces for equilibrium tie-lines is certainly a valid concern. When EPMA can be made at only a few points across the thickness of thin phases, this can result in inaccuracies in estimating tie-line compositions for these phases, since it is difficult to extrapolate to the interface based on so few data points. However, in most cases multiple diffusion paths could be evaluated, traversing a single phase under analysis from several different two-phase or three-phase fields. This gave a number of opportunities to measure phase composition. The composition variation in the thin phases (usually intermetallic compounds) is generally quite small, so that steep composition gradients are unlikely on the approach to a two-phase interface, reducing any likely errors, e.g., Fig. 3a. Also, with analyses made for two or three different temperatures, it is possible to compare the determined phase equilibria as a further check of consistency of the analyses. Based on the range of measurements made, most tie-line compositions can be assessed to be ±2 at.%.

One may be concerned about the X-ray absorption and fluorescence corrections in a composition gradient in diffusion multiples in contrast to a homogeneous phase for which the correction algorithms are originally developed. Although there is a jump of composition across a phase interface, the composition gradient in the phases approaching the interface is usually not very steep after a long-term anneal of the diffusion multiples. At low accelerating voltage and beam current, the X-ray generation volume can be reduced to 1 to 2 μm^3. The composition gradient in such small regions is usually negligible, allowing accurate absorption and fluorescence corrections to be made using existing algorithms.

4.3. Phase diagrams from equilibrated alloys—not *always* a gold standard

One would think that the equilibrated alloy method (melting, casting and heat treatment of individual alloys) is the ultimate "gold-standard" for equilibrium phase diagram determination. Usually this is true. However, since both the processes of solidification and heat treatment are involved, true equilibrium can be difficult to reach if the solid-state decomposition process is sluggish for some of the phases. An excellent example is shown in Fig. 9 which compares the 1000°C isothermal section of the Nb-Cr-Al ternary systems determined using individual alloys ((a) and (b)) and a diffusion multiple (c) [25–27]. Identical to the observations of Hunt and Raman [25] as well as Mahdouk and Gachon [26], the results from a diffusion multiple [27] showed that the Al addition stabilizes the high-temperature hexagonal C14-Laves phase of the binary Cr-Nb system ($NbCr_2$) to lower temperatures, and the solubility of Al in C14 is as high as ~45 at.%, which is consistent with previous observations [25, 26]. The composition of the C14-Laves phase was almost a ternary line-compound in the form of $Nb(Cr,Al)_2$. The diffusion-multiple results are consistent with the powder-metallurgy result of Mahdouk and Gachon [26], and these findings together suggest that the very wide (Nb variation) phase region of the C14-Laves reported by Hunt and Raman [25] is unrealistic. The apparent widening of the C14-Laves phase region in the case of Hunt and Raman was probably due to segregation during primary solidification of C14-Laves. The C14-Laves phase with composition away from $Nb(Cr,Al)_2$ formed during solidification and did not have sufficient time to decompose due to its sluggish kinetics. In the diffusion multiple, the C14-Laves phase formed at 1000°C by diffusion reactions, and it did not go through the solidification process; thus it is much easier to reach local equilibrium



(a)

(b)

(c)

Figure 9 Comparison of the 1000°C isothermal section of the Nb-Cr-Al ternary system: (a) an approximate phase diagram reported by Hunt and Raman [25] based on results from equilibrated alloys (phase boundaries and tie-triangles were not well defined), (b) results reported by Mahdouk and Gachon [26] again based on equilibrated alloys, and (c) results obtained from a diffusion multiple [27].

at the phase interfaces. In the case of Mahdouk and Gachon [26], the direct reaction calorimetry process involves fine powders that react together in the solid state, thus it also avoids the problem associated with melting and solidification. Comparison of the work of both Hunt and Raman [25] and Mahdouk and Gachon [26] is a great example to show that it is much easier to reach equilibrium by solid-state reactions than to go through a solidification and decomposition process when involving high-melting compounds and when the decomposition kinetics are sluggish. Both Hunt and Raman [25] and Mahdouk and Gachon [26] annealed their samples at 1000°C for 168 h (1 week). By comparison with the diffusion multiple approach, it appears that Mahdouk and Gachon reached equilibrium through solid-state (powder-metallurgy) reaction, whereas Hunt and Raman [25] did not reach equilibrium for the C14-Laves phase using melting/solidification and decomposition annealing.

This example clearly shows a possible advantage of the powder-metallurgy route in reaching equilibrium for very high temperature alloys. But the powder-metallurgy route also has its drawbacks. It is very easy to introduce oxides or nitrides or moisture at fine particle surfaces, thus contaminating the samples and potentially causing interstitial stabilization of

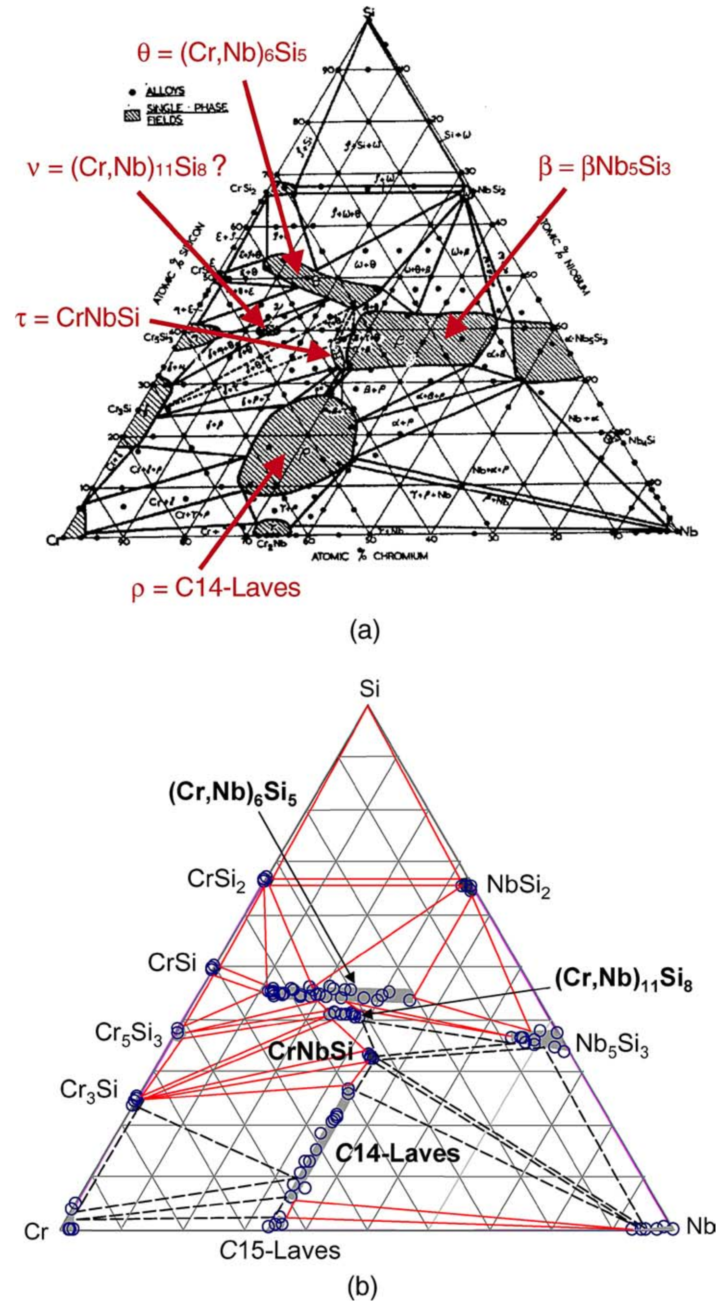


Figure 10 Comparison of the 1000°C isothermal section of the Nb-Cr-Si ternary system: (a) results obtained from 220 cast and annealed alloys (It is very likely this is not an equilibrium phase diagram because many alloys might not have reached equilibrium)[28], and (b) results obtained from a diffusion multiple [29].

non-equilibrium phases. The diffusion-multiple method can be superior in this regard—in that it does not undergo the solidification process and at the same time avoids potential interstitial contamination from powders. The phases formed with this method should be equilibrium phases, and local equilibrium at the phase interface would give the equilibrium phase diagram.

Most of the Nb-Cr-Al results obtained from the diffusion multiple (Fig. 9c) agreed well with those reported by Mahdouk and Gachon [26] except for the bcc(Nb) + C14-Laves + $Nb_2(Al,Cr)$ three-phase equilibrium. The diffusion-multiple results showed a much higher Al concentration in the C14-Laves phase in equilibrium with both bcc(Nb) and $Nb_2(Al,Cr)$. Several tie-lines in the bcc(Nb) + C14-Laves two-phase region and in the Nb_2Al + C14-Laves two-phase region clearly show the trend of high Al (>20 at.%) concentration in the C14-Laves phase in equilibrium with bcc(Nb) and Nb_2Al. In addition, a very low solubility of Cr in Nb_3Al was observed in the diffusion multiple, which is slightly different from the result of Mahdouk and Gachon [26], Fig. 9b. The limited thickness of the Nb_3Al and Nb_2Al phases, especially the Nb_3Al phase, may have introduced some error in the EPMA data obtained from the diffusion multiple and may have contributed to some of the difference in results between this study and that of Mahdouk and Gachon.

Another example is shown in Fig. 10 for the 1000°C isothermal section of the Nb-Cr-Si system [28, 29]. An isothermal section was constructed by Goldschmidt and Brand [28] based on results from 220 cast and annealed alloys (Fig. 10a). It is very likely that many of the alloys used by Goldschmidt and Brand had not reached equilibrium after only 336 h (2 weeks) anneal at 1000°C. Many Nb-base alloys, such as Nb-Ti-Si alloys studied by Bewlay *et al.* [30] and Nb-Hf-Si alloys studied by Zhao *et al.* [31], possess very slow kinetics, and thus they would not be at equilibrium after being annealed at 1000°C for only 336 h. For instance, even after annealing at 1500°C for 100 h, several Nb-Hf-Si alloys still had not reached full equilibrium [31]. It is very likely that the Nb-Cr-Si alloys would possess similar slow kinetics as well, thus the data reported in the phase diagram of Goldschmidt and Brand may not represent equilibrium conditions. This argument is supported by the fact the Nb_5Si_3 and Cr_3Si phases have very narrow composition ranges in the equilibrium binary phase diagrams [32, 33], whereas in the phase diagram presented by Goldschmidt and Brand, these phases show extensive composition ranges. This indicates that the decomposition process of the primary solidification structure was incomplete and equilibrium at 1000°C might not have been reached for many of their alloys. Goldschmidt and Brand reported a very large single-phase field for the β phase which they claimed to be the βNb_5Si_3 (high temperature form, stable only above 1645°C in the binary). This must be the primary solidification β-Nb_5Si_3 that has not yet been decomposed to the equilibrium phases at 1000°C. The α-Nb_5Si_3 extending from the Nb-Si binary is the low temperature $D8_l$ form. They also reported a Nb_4Si phase which is certainly not an equilibrium phase, since this phase does not appear in the Nb-Si equilibrium binary phase diagram. The very wide C14-Laves phase region (Fig. 10a) reported by them is also a good indication that the alloys around this region have not reached equilibrium. Under equilibrium conditions, the C14-Laves phase behaves like a ternary line compound with very little variation of Nb or Ti concentration, as shown in Figs 6b, 9b and 9c.

The 1000°C isothermal section of the Nb-Cr-Si ternary system, determined from a diffusion multiple, is shown in Fig. 10b [29]. The crystal structure of the θ-phase (Fig. 10a) reported by Goldschmidt and Brand is the same as that of $(Cr,Nb)_6Si_5$ (Fig. 10b), and the phases with which it is in equilibrium ($CrSi_2$, $NbSi_2$, CrSi, and Cr_5Si_3) were also observed in the diffusion multiple for $(Cr,Nb)_6Si_5$. Thus it is safe to conclude that their θ-phase is $(Cr,Nb)_6Si_5$. The composition of the θ-phase is off the stoichiometric composition of $(Cr,Nb)_6Si_5$, which may be due to the primary solidification segregation. The ν-phase (Fig. 10a) is very likely $(Cr,Nb)_{11}Si_8$. The crystal structure of the τ-phase is the same as that of CrNbSi, thus they are the same phase. Again the composition of the τ-phase is off the stoichiometry of CrNbSi probably due to the solidification segregation. The ρ-phase is certainly the C14-Laves $Nb(Cr,Si)_2$ which Goldschmidt and Brand already reported.

The equilibrium phase diagram (Fig. 10b), as determined with the diffusion-multiple approach, greatly helps to clarify the confusion in the phases of this ternary system and puts the phases at the right stoichiometric positions in the phase diagram. Without the diffusion-multiple results it would have been much harder to correlate the θ, ν and τ phases since their reported compositions did not correspond to the crystal structure stoichiometries. The work from diffusion multiples provides, for the first time, a much clearer picture of the phase equilibria in this very complex Nb-Cr-Si ternary system. This system also provides a good indication of the applicability of the diffusion-multiple approach in mapping very complex phase diagrams.

4.4. The usefulness of EBSD

EBSD [34] is an extremely useful tool for phase diagram mapping using diffusion multiples since some phases have compositions very close to one another and EPMA data alone would not be enough to differentiate them. For instance, the compositions of the phases $(Cr,Nb)_6Si_5$ and $(Cr,Nb)_{11}Si_8$ are very similar (Fig. 10b). Without EBSD it would require time-consuming transmission electron microscopy (TEM) and electron diffraction analysis to tell them apart. Also, the ternary NbCrSi phase sits right on the same Nb concentration as the C14-Laves phase; it would have been very easy to mistakenly plot the C14-Laves phase region (line) all the way to the NbCrSi composition. The EBSD results helped us correctly interpret the data. EBSD has been applied to determination of many phase diagrams using diffusion multiples.

4.5. Impurity-induced stabilization of metastable phases

If this happens, it should happen in equilibrated alloys too, since when the phases start to equilibrate following solidification segregation, the adjacent phases form a tiny diffusion couple and the interdiffusion process takes place during annealing. If an impurity induces stabilization of metastable phases in both the diffusion couples and diffusion multiples, it should also stabilize these phases in equilibrated alloys if the impurity level is the same in the diffusion couples/multiples and the equilibrated alloys. The key is to keep impurities as low as possible in both equilibrated alloys and diffusion multiples. Interstitial contamination might have been a problem for systems such as Nb-Cr-Si and Nb-Ti-Al, but by careful design of the diffusion multiples, it was possible to effectively reduce the interstitial contamination.

4.6. Missing phase situations

In rare occasions, one of the phases may not form by interdiffusion reactions in diffusion couples, which makes one wonder whether a similar situation might happen in diffusion multiples. An “infamous” example is the Ti-Al binary system [35]. When Ti/Al diffusion couples were made, only the $TiAl_3$ phase was found, but when Ti/$TiAl_3$ diffusion couples were made, all the compounds appeared [35]. Interestingly, in one of

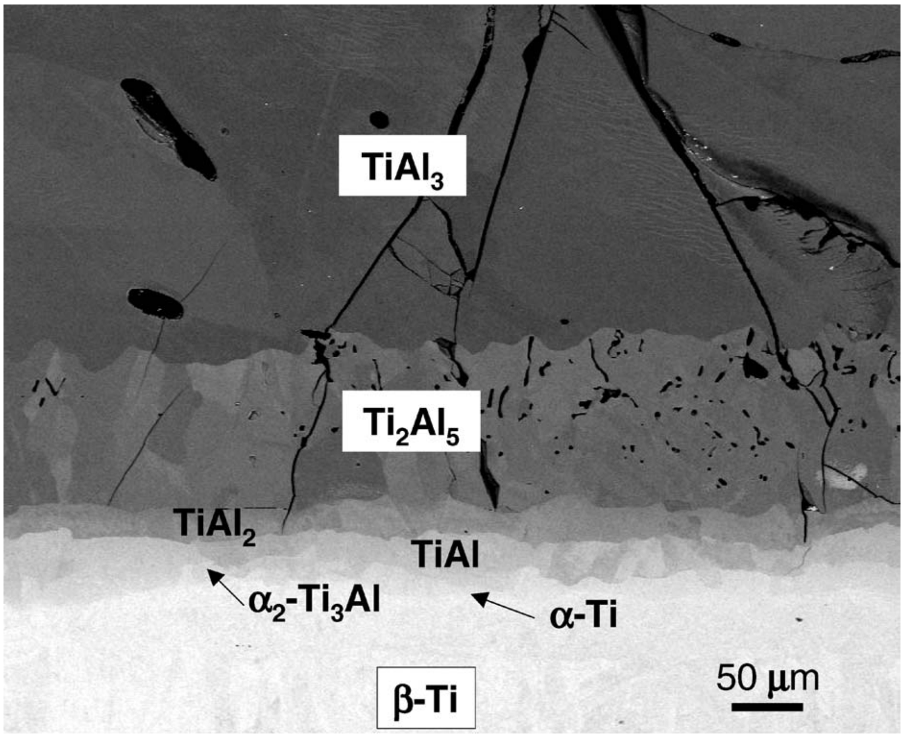


Figure 11 Backscatter electron SEM image of the Ti-TiAl$_3$ binary area of a diffusion multiple annealed at 1000°C for 2000 h showing the formation of all the Ti aluminides [21]. The interface between the α-Ti and β-Ti phases cannot be seen due to small difference in their average atomic number, they can be easily differentiated with EBSD.

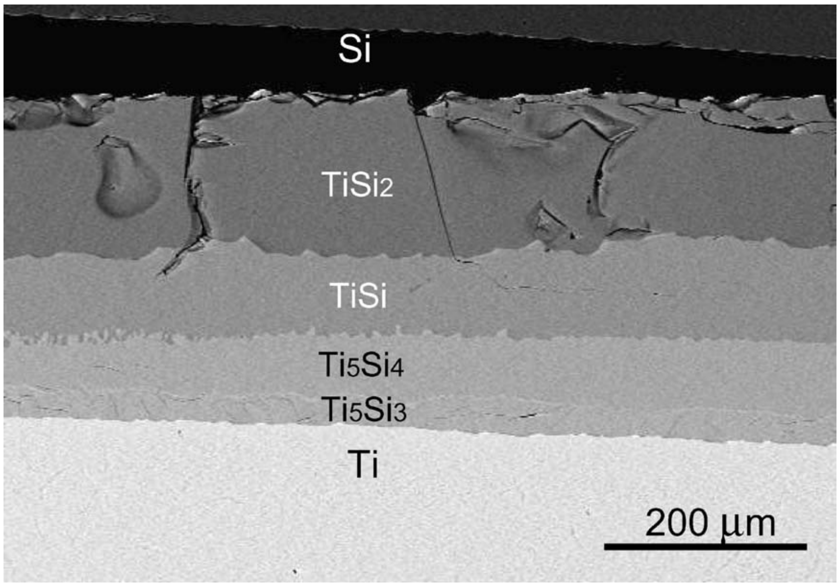


Figure 12 Backscatter electron SEM image of the Ti-Si binary area of a diffusion multiple annealed at 1150°C for 2000 h showing the formation of all the Ti silicides [36].

the diffusion multiples studied, there happened to be a Ti/TiAl$_3$ diffusion couple. All the intermetallic compounds/phases were found to have formed by interdiffusion reaction, as shown in Fig. 11 [21]. Similarly all the compounds were found to have formed between Ti and Si as shown in Fig. 12 [36]. These stoichiometric silicides are supposed to be difficult to form by interdiffusion, yet all of them appeared. A close examination of the cases reported with missing phases in diffusion couples shows that in most such cases equilibration was attempted at temperatures below half of the homologous melting points, although the exact reason for non-occurrence of phases under these conditions is still not well understood. All the recent phase diagram determination work using diffusion multiples has been concentrated on high temperatures. That may be the reason that we have not seen a missing phase situation. Even though non-occurrence of phases was very rare, when using diffusion couples and diffusion multiples in determining phase diagrams one should always be watchful for the possibility of missing phases (especially at low temperatures). In the cases reported in this paper, it is highly likely that the phase diagrams obtained are equilibrium ones, since all the binary phases appeared and all the confirmed ternary compounds were observed. It is always a good check to see whether all the binary phases and reported ternary phases appear.

In the case of a missing phase, the data obtained would be metastable equilibrium; i.e., true equilibrium but with the missing phases removed from the free energy minimization process. Rules exist regarding the location of the phase boundaries in such cases. For instance, the solubility of phases increases when a phase is missing and lines on a ternary isothermal section would extend smoothly into the metastable region. Such metastable phase equilibria can be exposed by comparing the results with well-established binary phase diagrams.

Although the diffusion-multiple technique is a unique and powerful tool in determining phase diagrams, it is especially useful in conjunction with other methods. In order to check the reliability of the information obtained about the ternary and higher-order phase diagrams, a combination of the diffusion-multiple technique with an investigation of selected equilibrated alloys is desirable, especially for the regions where the exact phase boundaries are in question.

One should be extremely cautious when applying the diffusion-multiple approach to phase diagram determination at relatively low temperatures. At low temperatures, the diffusion rates are low and the formation of intermetallic compounds (especially high melting-point ones) becomes very difficult kinetically. The formation of high melting-point compounds also hinders further diffusion of the elements, potentially resulting in missing phase situations. It is strongly recommended that the diffusion-multiple approach be applied only to temperatures above half of the homologous melting points. To determine phase diagrams at relatively low temperatures, the CPD approach [10] and other thin film deposition techniques are advantageous since much less time is required to form a homogeneous composition across the thin film thickness. This is particularly true when the substrate is heated to the desired temperatures during thin film deposition. The traditional equilibrated alloy approach is also preferred at low temperatures—ample annealing time should be given to warrant equilibrium though.

5. Concluding remarks

The results presented in this paper clearly show that the data obtained from diffusion multiples are in very good agreement with reliable literature data obtained from equilibrated alloys. Such agreement serves as a good indication of the reliability of the phase equilibrium information from diffusion multiples.

The combination of the use of diffusion multiples with results on selected equilibrated alloys would be a good safety check against any potential occurrences of metastable or missing phases. Phase diagrams mapped at two or more temperatures are also very useful to check the consistency and reliability of the results. In addition, it would also be useful to study diffusion multiples annealed at one temperature for different periods of time to check the consistency of phase presence.

So far no missing phase situation has been encountered. Nevertheless, care should always be taken to make sure all the binary compounds and ternary compounds reported from conventional experiments appear in the diffusion multiple.

The EBSD method is extremely useful in phase diagram mapping using diffusion multiples for crystal structure identification.

The success of mapping very complex phase diagrams such as Nb-Cr-Si and Nb-Ti-Al using diffusion multiples is extremely encouraging.

No method is fool-proof. One needs to be watchful for potential pitfalls for each method, including the "gold-standard" equilibrated-alloy method where ample time should be used to ensure the alloys reach equilibrium conditions.

It can be seen that careful use of the diffusion-multiple approach can achieve orders of magnitude higher efficiency in phase diagram mapping without sacrificing the quality of the data.

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