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Geometrical Approach to Reaction Schemes of Multicomponent Phase Diagrams

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A unique method for describing and establishing the reaction scheme of a multicomponent phase diagram is proposed in terms of graph theory. A geometrical representation of the connections between invariant reactions is considered as the basis to introduce the matrix formula of a graph that models a reaction scheme; then the number of all possible reaction schemes is enumerated. With a matrix operation, the most probable (full or partial) reaction scheme(s) can be selected within available experimental data. A ternary phase diagram was chosen as an example to show how to relate with experimental data. It is also shown that the number of invariant reactions in a ternary phase diagram can be expressed as a function of the numbers of binary and ternary phases.

Keywords graph theory, monovariant reaction, phase equilibria, phase rule, Scheil reaction scheme, theory and modeling

1. Introduction

Various techniques for microstructural control can be applied to alloys composed of various elements due to their higher degree of freedom affecting phase equilibria in multicomponent phase diagrams. Therefore, for establishing a suitable heat-treatment process for a certain alloy system, a temperature-composition phase diagram shows the phases of components, and this will provide information to control the microstructural evolution process of alloys. Although various phase diagram calculation methods have been developed and progressed, such as Calphad-type methods or first principle calculation methods, their applications are still limited due to the difficulties in evaluating the thermodynamic properties of phases. Therefore, the importance of experimental work is still important for the establishment of phase diagrams. However, it is generally very difficult, elusive, and time-consuming to develop even a part of an isothermal or isoplethal section of a ternary phase diagram. The difficulties are caused by not only the complicated relationship among phases at each temperature (an isothermal section) but also by the complicated relationship between isothermal sections in a high dimensional space even under a constant pressure condition.

Reaction schemes (Scheil reaction schemes) or flow diagrams have been used to simplify the presentation of complex multicomponent diagrams [1994Con]. With an established reaction scheme, an equilibrium ternary or multicomponent phase diagram is more easily constructed through experimental work. However, it is not easy to manage and evaluate the reliability of the reaction scheme because even the number of candidates for a reaction scheme is not known.

The aim of this study is to apply graph theory for the description of reaction schemes. It will be shown that this mathematical expression enables one to take into account all the available but fragmentary data obtained by various and individual experiments for construction and evaluation of a reaction scheme. In this article, a ternary phase diagram at a certain pressure is picked as an example.

2. Outline of the Mathematical Method

2.1 Description of a Reaction Scheme in Terms of Graph Theory

According to Gibbs Phase Rule, it is deduced that four is the maximum number of phases coexisting at a highest-order equilibrium (i.e., an invariant reaction) in any ternary system at constant temperature and constant pressure. In a reaction scheme, each invariant reaction is connected to "monovariant lines" that represent the next highest-order equilibrium among three phases chosen from four phases related to the corresponding invariant reaction. That is to say, a reaction scheme for a ternary phase diagram accounts for the interrelations among three- and four-phase equilibria. The number of next highest-order equilibria related to an invariant reaction can be counted to be:

$$\binom{4}{3} = 4$$

Therefore, each invariant reaction can be expressed as a point where four monovariant lines flow in or out. Figure

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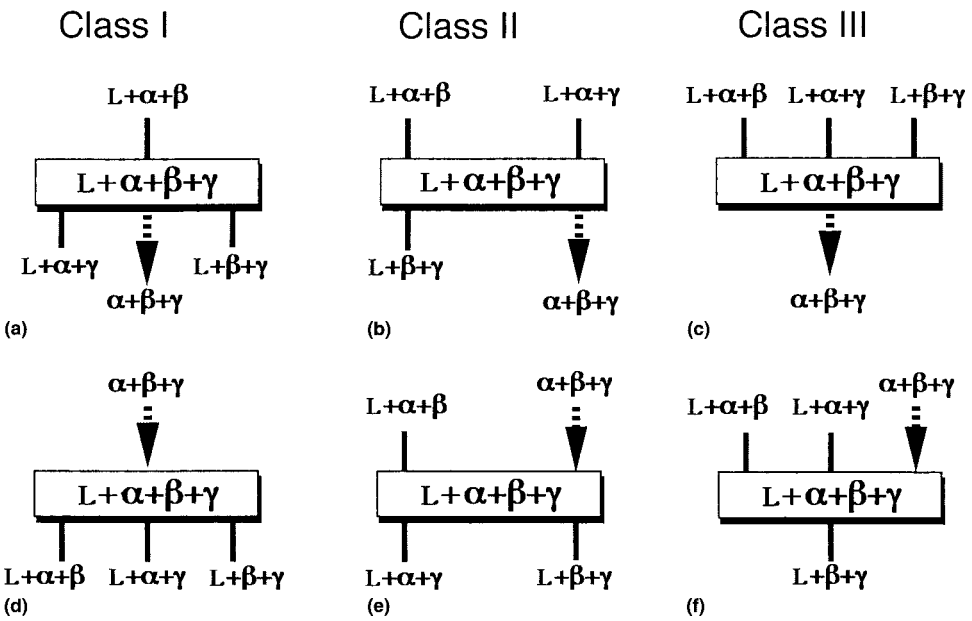

Fig. 1 Six classes of four-phase equilibrium as examples: (a) pattern containing three flow lines flowing into and a Class I ternary four-phase equilibrium, i.e., ternary eutectic; (b) pattern containing two flow lines flowing into and a Class II ternary four-phase equilibrium; (c) pattern containing one flow line flowing into and a Class III ternary four-phase equilibrium, i.e., ternary peritectic; (d) exclusive class for the four-phase equilibrium in the ternary phase diagram; (e) example of metatectic reaction in ternary phase diagram; and (f) other example of metatectic reaction in ternary phase diagram.

1 shows such relationships among a liquid phase and three solid phases. Monovariant lines including a liquid phase are referred to as 'flow lines" or 'flow pipes."

Theoretically, there are 25 kinds of invariant reactions for ternary systems [1966Pri], and each next highest-order equilibrium originates a binary or a pseudobinary phase diagram regardless of whether it is a eutectic, a peritectic, a eutectoid, or another reaction, or a ternary invariant reaction. The authors applied graph theory to reaction schemes, in which every invariant reaction includes one liquid phase and three different solid phases, shown in Fig. 1. Ternary peritectic reactions are (a) and (b), eutectic reaction is (c), and (e) and (f) are remelting reactions in ternary system, respectively, but (d) is a forbidden reaction. With these invariant reactions, one can describe the connection of flow lines that are monovariant reactions.

Figure 2 shows (a) a flow-line network in a ternary phase diagram, (b) a part of the corresponding reaction scheme, and (c) its topological expression. Invariant reactions are represented by points (No. 17-22) connected with four other points. Each of the ternary invariant reactions is accompanied with a three-solid phase field (No. 28-33), which appears in the isothermal section of the ternary phase diagram at low temperature, as shown in Fig. 2(d). Therefore, in such a simple ternary phase diagram, solid phases related to an invariant reaction correspond to the phases appearing in the three-solid phase field. Then, a set of phases related to each of four monovariant lines can be deduced by choosing three phases out of four. Therefore, a common monovariant reaction connects two invariant reactions.

Solid lines start from binary invariant reactions (No. 1-8). In some of the ternary phase diagrams pseudobinary invariant reactions appear between invariant reactions [1995Vil, 2001Miu]. Figure 3 shows a schematic drawing of a pseudo-binary reaction found in the Ni-Al-Zr system just beside the Ni-Zr binary edge [2001Miu]. The possible pseudobinary invariant reactions are represented by points (No. 9-16, 23-27) in Fig. 2(b). Such reactions are quite few in number, but they significantly affect solute distributions in the microstructure during solidification; this may cause cracking of products formed by casting.

As can be seen in Fig. 2, monovariant reactions connect all of the invariant reactions, including binary and pseudo-binary reactions. Therefore, a mathematical way to express connection of neighboring points is useful for representing a reaction scheme. In graph theory, a network is described so that the lines called edges are connected at points called vertices, as can be seen in Fig. 4 [1967Kau]. A graph is an abstract object, but graphs can be used to represent structures of quite diverse nature, such as electric circuits, the rules of certain games such as chess or checkers, the ranking of participants on a tournament, etc. [1972Gar]. Therefore, graph theory is suitable for expressing reaction schemes as graphs in which vertices and edges correspond to invariant reactions and flow lines, respectively.

A reaction scheme represents the relation among invariant reaction temperatures by oriented lines connected at two invariant reactions to show which reaction occurs at a higher temperature. To describe a realistic reaction scheme for a ternary phase diagram, a concept of oriented (direct)

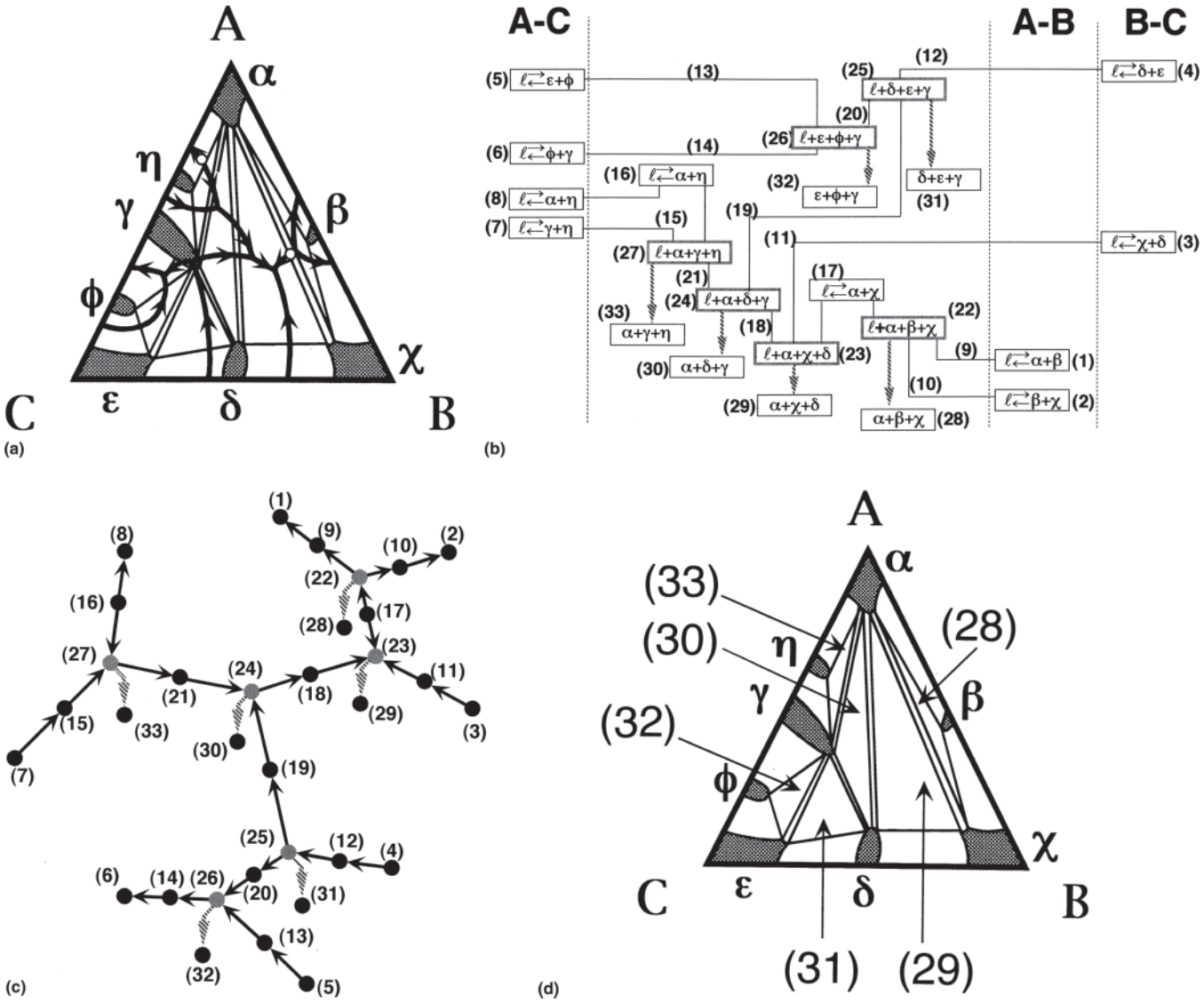

Fig. 2 (a) Example of the flow-line network in a ternary phase diagram. (b) Interconnection of flow lines shown as a part of the geometrically transformed phase diagram. (c) Network of flow lines and vertices, which correspond to ternary, binary, and pseudo-binary invariant reactions. (d) Isothermal section of the ternary phase diagram at low temperature.

graph is introduced to take the invariant reaction temperature into account. Illustrated in Fig. 4 is a concept of an oriented graph [1967KAU, 1972GAR]. In an oriented graph, each edge is represented by a line with an arrow to indicate its orientation (Fig. 4a). The existence of arrows is expressed as $a_{ij} = 1$, which means that an edge connecting two vertices i and j is oriented a way from vertex i toward vertex j. As presented in Fig. 4 (b), a set of a_{ij} forms an adjacency matrix R for an oriented graph, which expresses the interrelation between vertices. Figure 4(c) is an adjacency matrix expression of the flow lines in the reaction scheme shown in Fig. 2(c). It is obvious that there is no inconsistency between the reaction scheme and the matrix representation. We can conclude that an adjacency matrix R completely expresses a reaction scheme.

2.2 Expression of a Reaction Scheme of a Ternary Phase Diagram in Terms of Graph Theory

It is shown in Sec. 2.1 that the reaction scheme of a phase diagram of concern is developed by taking the relationship among the invariant reaction temperatures into account. All candidates should be examined to obtain the most rational, appropriate reaction scheme. Therefore, as the basis, all of the possible adjacency matrices R, as the candidates for the reaction scheme, are needed. For such a purpose, the numbers of monovariant, invariant, and pseudo-invariant reactions are required because the numbers of the reactions in any ternary phase diagrams can be decided by Euler's theorem on polyhedra, as a function of the number of phases.

As mentioned above, in the simplest case consisting of only ternary eutectic and/or peritectic reactions, each three-

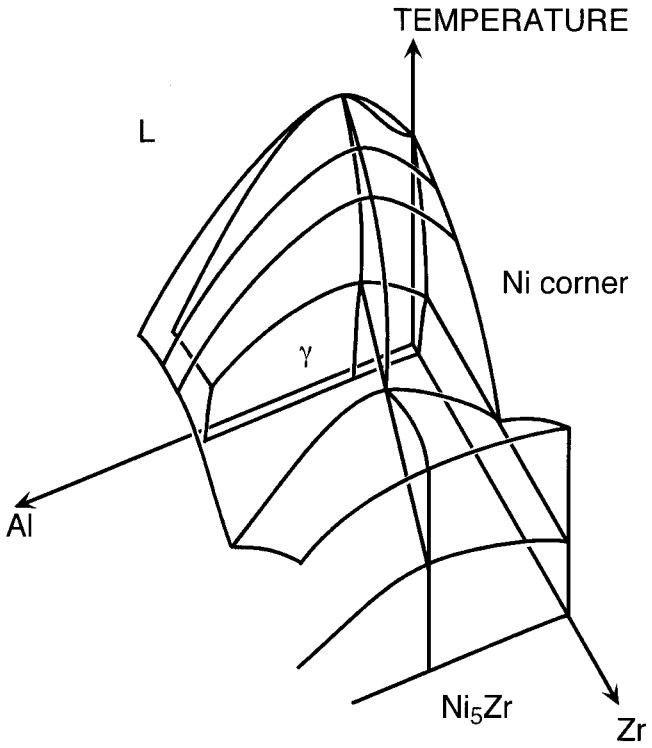

Fig. 3 Schematic drawing of Ni-Al-Zr phase diagram near Ni-Zr binary edge, which includes a pseudobinary invariant reaction appearing as a ridge between the binary invariant reaction on Ni-Zr binary edge and the ternary invariant reaction

solid phase field existing in an isothermal section at a low temperature corresponds to a four-phase equilibrium. Therefore, the number of three-phase equilibria is needed. Figure 5(a) shows a schematic projection of such a ternary system with eight phases, and Fig. 5(b) shows an 8th convex polygon as a simplified expression of the ternary phase diagram shown in Fig. 5(a). Through this operation, the compositional information such as the solubility of elements in phases and the width of each two-phase regions are lost. An *n*th polygon can be divided into a number of triangles as shown by examples in Fig. 5(c) for the case of $n = 8$. This operation is termed "triangulation" or "simplicial decomposition." Each of the triangles represents a three-solid phase field. A similar method was also proposed by Slyusarenko et al. [1999Slu, 2001Sof] for the representation of phase relationships in isothermal sections of multicomponent systems in terms of the graph method.

In Fig. 5(c), apices, sides, and triangles in the *n*th polygon correspond to an invariant reaction in binary, pseudobinary, and ternary systems, respectively. The number of each of them is needed as a function of *n* for applying the concept for the description of the reaction schemes in the form of the adjacency matrix. By Euler's theorem [1997Fur] on polyhedra (Appendix 1), it can be deduced that the numbers of sides, diagonal lines, and triangles are n, $(n - 3)$, and $(n - 2)$, respectively, in any case. The number of vertices between binary and neighboring ternary invariant reactions is n, which also corresponds to possible pseudobinary reactions, as is observed in the Ni-Al-Zr system shown in Fig. 3 [2001Miu]. Thus, the number of vertices in an adjacency matrix R for an *n*th polygon:

$$n + n + (n - 3) + (n - 2) = 4n - 5 \quad \text{(Eq 1)}$$

Therefore, we should consider an adjacency matrix R of $[(4n - 5) \times (4n - 5)]$ to describe the relation among $(4n - 5)$ vertices in any of the reaction schemes for the *n*th polygon completely. The number of vertices $(4n - 5)$ is 27 for the case $n = 8$, and the adjacency matrix R is (27×27) in size. Each of No. 28-32 corresponds to a three-solid phase field, not an invariant reaction. An adjacency matrix R shown in Fig. 4(c) corresponds to a ternary phase diagram shown in Fig. 2.

For ternary phase diagrams having several ternary compounds, a similar mathematical treatment can be accomplished by extending the above discussion. The ternary phase diagram with a ternary compound is represented by an *n*th polygon having a point inside. As this point is a component of ternary phase equilibria, it is necessary to take it into account for the triangulation of the geometrical figure shown in Fig. 6. Similarly the number of sides, diagonal lines, and triangles can be deduced by Euler's theorem on polyhedra (Appendix 2 [1997Fur]). Those are n, $(3m + n - 3)$ and $(2m + n - 2)$, respectively, for a ternary system with m of ternary compounds. Therefore, one should consider an adjacency matrix R of $[(5m + 4n - 5) \times (5m + 4n - 5)]$.

2.3 Inspection of Paths Among Vertices by Operation of an Adjacency Matrix for Establishing a Reaction Sheme

As mentioned above, the numbers of phases, n and m, are the keys to the adjacency matrix expression. We shall discuss the simplest case without ternary compounds in detail. In the case, there are $(4n - 6)$ edges corresponding to the monovariant lines in the ternary system with n of phases. Therefore, an adjacency matrix R of $[(4n - 5) \times (4n - 5)]$ is filled with $(4n - 6)$ of numeral 1 and the rest are all numeral 0 to represent a reaction scheme. Then, all of the hypothetical reaction schemes can be provided by filling each of a_{ij} by $(4n - 6)$ of numeral 1 (see Appendix 3 for detail).

For the establishment of the reaction scheme of concern, it is necessary to present the relationship among all the invariant reactions, not only between the neighboring ones. To investigate connections from one invariant reaction to the others through several invariant reactions, multiplication of an adjacency matrix R for an oriented graph is useful. A matrix R^2 $(= R \times R)$ has a set of elements a'_{ij}:

$$a'_{ij} = \sum_h (a_{ih} \times a_{hj}) \quad \text{(Eq 2)}$$

If both a_{ih} and a_{kj} in the adjacency matrix R are 1 for a certain vertex h, $a'_{ij} = 1$, and vertices i and j are connected

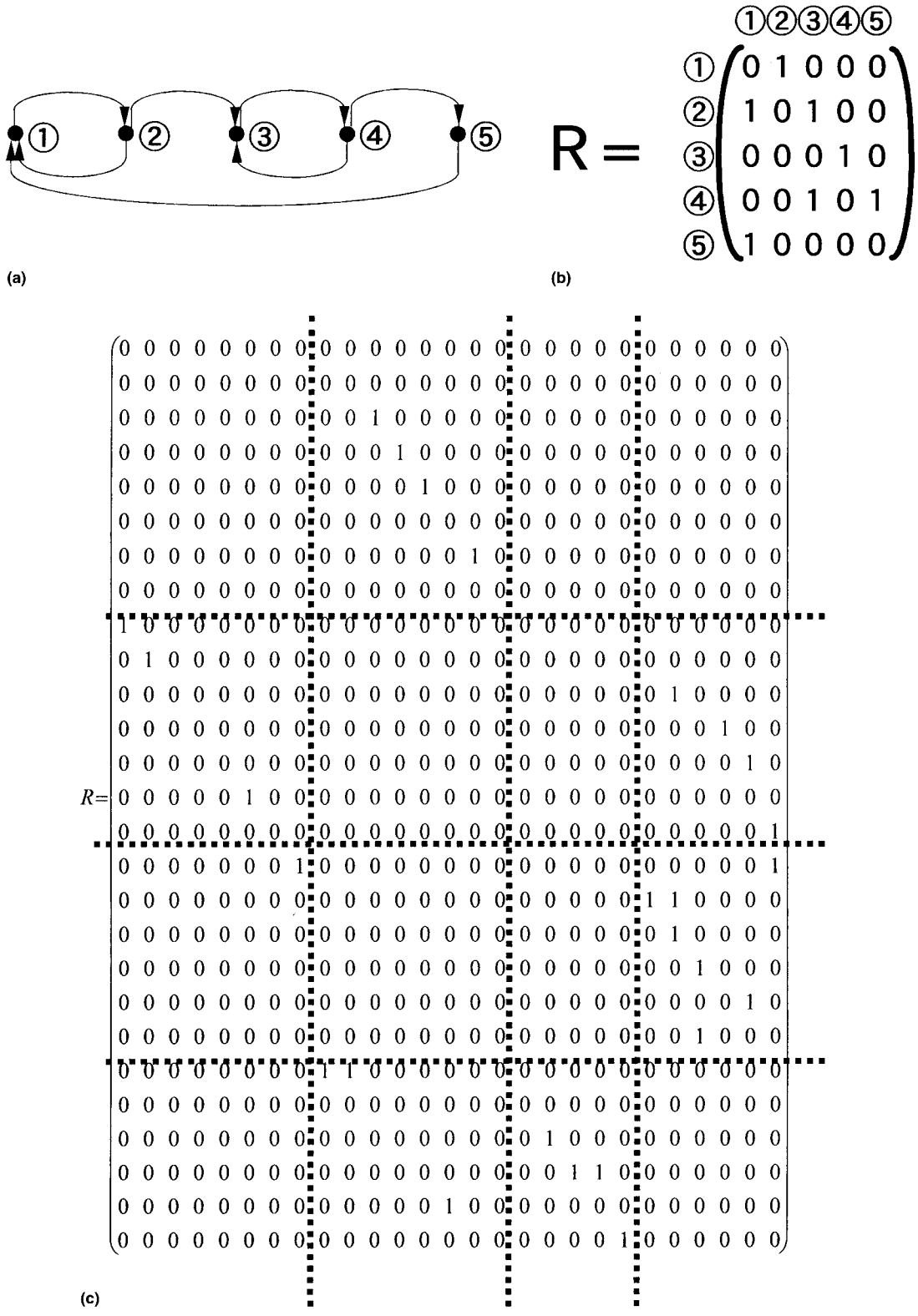

Fig. 4 (a) Oriented graph and (b) corresponding adjacency matrix *R*. (c) Adjacency matrix expression of the phase diagram shown in Fig. 2

by two edges via the vertex *h* (Fig. 7). In the matrix R^2, $a_{13} = 1$. This means there is a route from vertex 1 to vertex 3 through two of oriented edges. The *k*th power of the adjacency matrix *R*, R^k, provides information whether the graph has a path from one vertex to another through *k* of oriented edges. This idea enables one to examine whether

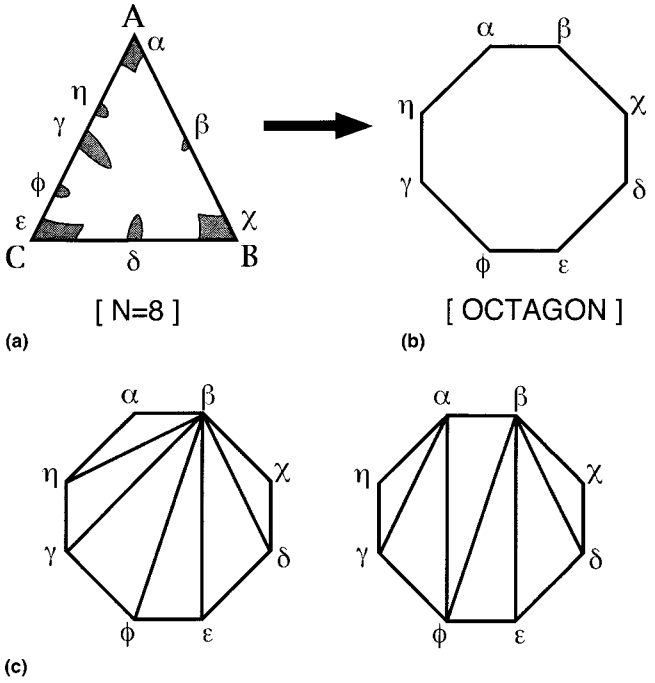

Fig. 5 (a) Example of a ternary phase diagram with 8 of binary invariant reactions with no ternary compound. (b) A ternary phase diagram transformed geometrically to an 8th convex polygon, i.e., an octagon. (c) Examples of triangulated patterns of an octagon.

a certain invariant reaction is located downstream of another invariant reaction in a reaction scheme. For such a purpose a matrix S provided by following method is useful:

$$S = R + R^2 + R^3 + R^4 + \cdots + R^{k_{max}} = \sum_{k=1}^{k_{max}} R^k \qquad \text{(Eq 3)}$$

where $k_{max} = (n - 2) \times 2 + 2 = (2n - 2)$ for any nth polygons, which is calculated from numbers of ternary invariant reactions and pseudobinary reactions. Hereafter, the matrix S is referred to as an integrated adjacency matrix. Figure 8 represents the integrated adjacency matrix S corresponding to the reaction scheme shown in Fig. 2. An element $a_{ij} = 1$ in the integrated adjacency matrix S means the temperature for an invariant reaction represented by vertex i is higher than that represented by vertex j in a reaction scheme. Once an adjacency matrix R is given, the integrated adjacency matrix S can be obtained by matrix operation.

It is obvious that such comparisons between the elements a_{ij} in the integrated adjacency matrix S and experimental data enables us to take all information into account for excluding improper adjacency matrices. Then the most promising reaction scheme can be selected in conjunction with binary phase diagrams and fragmentary ternary data sets obtained by experimental studies.

3. Discussion

3.1 Enumeration of the Number of the Candidates

It was shown that the proposed mathematical expression enables us not only to model but also to construct the reaction scheme easily at least for the simplest case. The most important thing is that information on phase relations, especially reaction temperatures, can be taken into account for the construction of the reaction scheme through this method. Although this has been accomplished for the establishment of various phase diagrams by hand, the advantage of the proposed method will be realized when the number of candidates for the reaction scheme of the simplest ternary phase diagram with n of binary invariant reactions is evaluated.

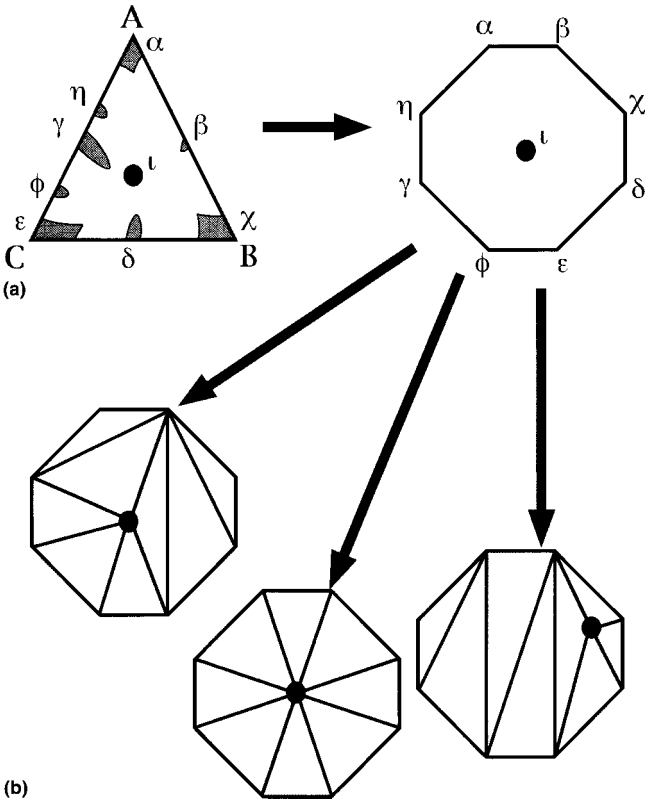

Fig. 6 (a) Schematic drawing of a ternary phase diagram with a ternary compound and (b) corresponding polygon and some examples of triangulated patterns

If there is no information on phase equilibria related to the invariant reactions, all kinds of triangulated patterns must be generated for a ternary phase diagram to provide a hypothetical reaction scheme. There is a large number of ways to triangulate a polygon, and each of the triangulated patterns includes various kinds of the adjacency matrices R as candidates for the reaction scheme. The number of triangulation patterns of nth polygon is known as Catharan number, D, expressed by [1983POL]:

$$D = \prod_{s=3}^{n} \left(\frac{4s - 10}{s - 1} \right) = \left(\frac{2}{2} \right) \left(\frac{6}{3} \right) \cdots \left(\frac{4n - 10}{n - 1} \right) \qquad \text{(Eq 4)}$$

Each of the triangulated patterns corresponds to a particular graph with $(4n - 5)$ vertices connected by $(4n - 6)$ edges. By orienting each edge in a systematic manner, all

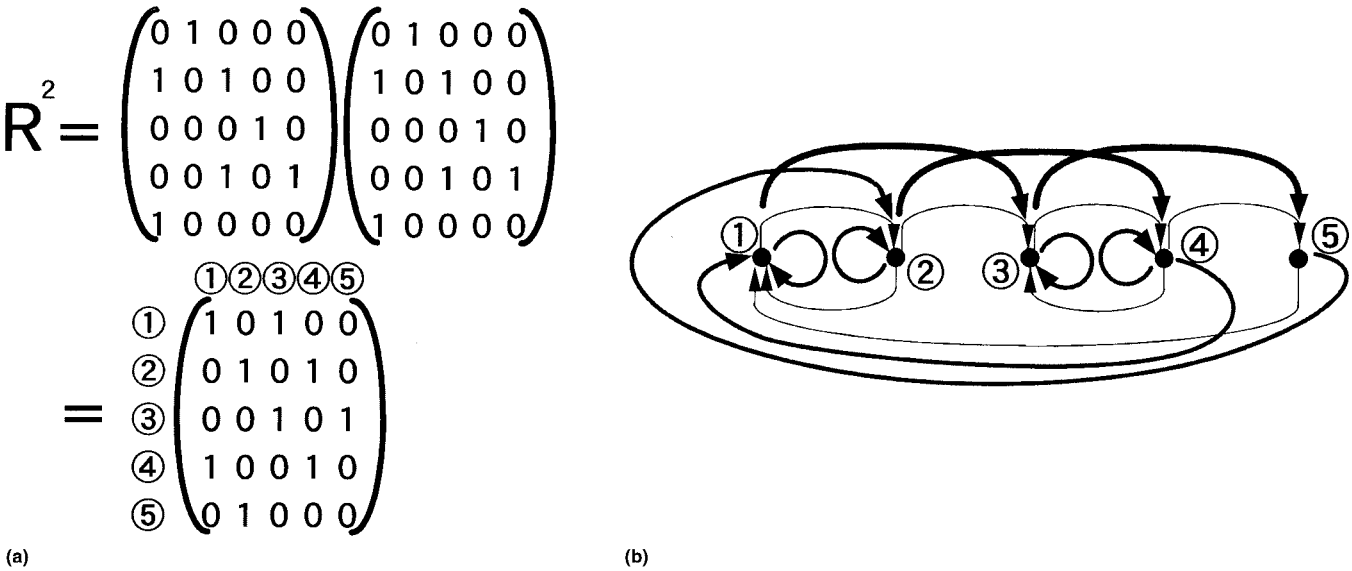

Fig. 7 (a) Multiplication of the adjacency matrix *R* and (b) corresponding oriented graph

hypothetical reaction schemes can be provided and then easily expressed in the form of the adjacency matrix. Therefore, there are $2^{(4n-6)}$ oriented graphs for each of the triangulation patterns. On the other hand, as the combination of flow lines at a ternary invariant reaction, three monovariants, each of which includes one liquid phase, are not allowed to flow out from an invariant reaction because it corresponds to the case represented by Fig. 1(d). Moreover, pseudobinary reactions also must consist of arrows having a suitable orientation. The number of candidates including these forbidden invariant reactions are, however, not so large compared with $2^{(4n-6)}$, and these can be expelled by applying suitable rules.

Although some of the adjacency matrices *R* may include some not-appropriate reactions, the total number of hypothetical reaction schemes, *P*, can be expressed:

$$P = D \times [2^{(4n-6)}] = \prod_{s=3}^{n} \left(\frac{4s-10}{s-1} \right) \times 2^{(4n-6)} \qquad \text{(Eq 5)}$$

Table 1 shows *D*, $2^{(4n-6)}$, and *P* as functions of *n*. With increasing *n*, *P* increases abruptly, and it becomes harder to provide and examine all of the hypothetical reaction schemes by hand. On the other hand, the mathematical method proposed in this article enables us to handle all candidates automatically. An important thing to note is the present method is easily programmed for a computer. The production method of all hypothetical adjacency matrices *R* has an iterative nature, shown in Appendix 3. An adjacency matrix *R* including inappropriate reactions can be excluded by applying simple rules. The integrated adjacency matrix *S* with which the examination becomes easier can be deduced by a simple way as expressed by Eq 2 and 3. Computer power is currently increasing rapidly, and this method can be turned to an advantage.

Some shortcuts for the reduction of the number of candidates are of great help to a practical calculation. One of them is to disregard the pseudobinary invariant reactions. The pseudobinary invariant reactions are found only infrequently. This results in the large reduction of the number of vertices, i.e., $(2n - 3)$. The total number of the hypothetical reaction schemes for this case, P', is also in Table 1. P' is much smaller than *P*. However, one may miss the existing pseudobinary reactions. A pseudobinary invariant reaction near the binary edge is rare, but it may change the solidification sequence and solute distributions, which may result in cracking of the products. Moreover, if one a pseudobinary reaction is missed and is not taken into account, this may result in a serious disadvantage for the evaluation of thermodynamic parameters. As pseudobinary reactions are saddle points, they divide a reaction scheme into several parts. The reaction temperatures of invariant reactions neighboring a saddle point are both lower than that of the saddle point. Therefore, information on reaction tem-

Table 1 Numbers of the candidate for a ternary phase diagram as a function of the number of phases

n	*D*	$2^{(4n-6)}$	*P*	$2^{(2n-3)}$	*P′*
3	1	64	64	8	8
4	2	1,024	2,048	32	64
5	5	16,384	81,920	128	640
6	14	262,144	3,670,016	512	7,168
7	42	4,194,304	176,160,768	2,048	86,016
8	132	67,108,864	8,858,370,048	8,192	1,081,344

Note: Each of the numbers of triangulation patterns of *n*th polygon known as Catharan number *D*, combination of oriented edges $2^{(4n-6)}$, and the total of candidates for a ternary phase diagram P ($= D \times 2^{(4n-6)}$) are listed as a function of the number of binary phases *n* for a ternary phase diagram without ternary compounds. The total number of candidates for a ternary phase diagram without pseudo-binary reactions, P' ($= D \times 2^{(2n-3)}$), is also shown.

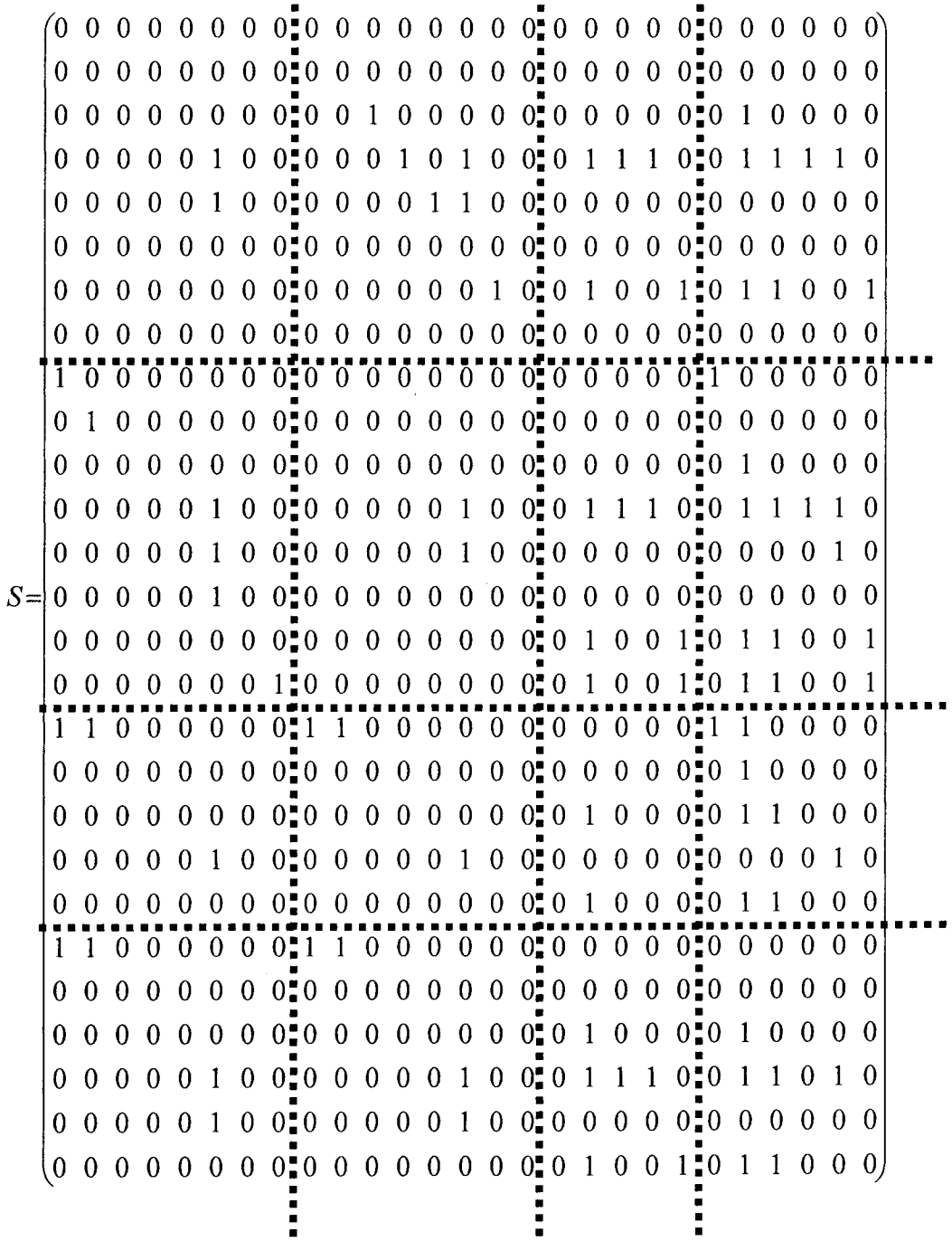

Fig. 8 Integrated adjacency matrix *S* corresponding to the reaction scheme shown in Fig. 2

peratures belonging to a part of the reaction scheme cannot be used to examine another part. This may affect a practical examination sequence.

Other kinds of invariant reactions such as monotectic reactions can be treated within the proposed method of this article in terms of graph theory; however, this may require some additional considerations. Similarly, the invariant reactions related only to solid phases, such as eutectoid and peritectoid reactions, can be addressed by the present mathematical methods. These will be discussed soon in other papers.

3.2 Higher-Order Multicomponent Phase Diagrams

A comment must be made on the extension of the present method to higher-order multicomponent phase diagrams. Although the explanation starts with ternary phase diagrams, essential points are common for all multicomponent

systems regardless of the number of components. This is because the invariant reactions in any multicomponent phase diagrams are connected with each other by monovariant reactions, the number of which is decided by the phase rule. In a K-component system, the number of phases coexisting at the highest order phase equilibrium is $(K + 1)$. Therefore, the number of mono-variant reactions connected to an invariant reaction is:

$$\binom{K+1}{K} = K + 1$$

The difficulty seems to lie in finding practical methods for estimating the number of invariant reactions associated with K-solid phase fields in the K-component system.

As mentioned above, an isothermal section of a ternary phase diagram transformed to an nth polygon can be triangulated to enumerate the number of invariant reactions. It is guaranteed by the correspondence of the spatial configuration of a next-highest order equilibrium, which is a three-phase equilibrium, to a simplex in the dimensional space of concern, which is a triangle in two-dimensional space. A quaternary phase diagram at a certain temperature is generally displayed by a tetrahedron in three-dimensional space. It corresponds to an isothermal section of a ternary system. The quaternary phase diagram at a certain temperature consists of various kinds of tetrahedrons composed of four phases at their corners. These tetrahedrons correspond to the monovariant lines in the quaternary systems. To count the number of quaternary invariant reactions, a way should be proposed for dividing an nth convex polyhedron, which models a quaternary phase diagram into a number of tetrahedrons, or "tetrahedrization." Besides, through an analogy, simplices in (K-1)-dimensional space through a simplicial decomposition, i.e., a triangulation in (K-1)-dimensional space, enable ones to treat higher-order multicomponent phase diagrams with K components (K-component system) in the same manner as that described here. This extended idea still has its basis only in the relationship between the phase rule and geometry.

4. Concluding Remarks

A mathematical expression of the reaction scheme of a ternary phase diagram is proposed in terms of graph theory. It was shown that an adjacency matrix R for an oriented graph represents a reaction scheme. An integrated adjacency matrix S provided by matrix operation of an adjacency matrix R represents relations among invariant reaction temperatures of a corresponding reaction scheme.

The size of the adjacency matrix is expressed as a function of the numbers of binary and ternary phases in a ternary phase diagram of concern. Then the number of hypothetical reaction schemes is derived by the Catheran number D and a concept of the oriented graph. Although the total number of hypothetical reaction schemes P increases abruptly with increasing the number of binary phases n the present method provides all of the candidates in the form of the adjacency matrix R in a systematic manner. Moreover the integrated adjacency matrix S can be used to examine the adjacency matrix R by comparison with experimental results including binary phase diagram data. The proposed method will provide a better prospect for the construction of higher-order multicomponent phase diagram based on experimental work.

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Appendix 1. The Number of Triangles in a Triangulated Polygon without Points: Futura's Application of Euler's Theorem

It was shown by Furuta that the triangulation of an nth convex polygon can be considered as follows [1997Fur]. According to Euler's theorem on polyhedra:

$$g - h + v = 1 \qquad \text{(Eq A1.1)}$$

where g is the number of points, h the number of sides and diagonal lines, and v the number of faces. In this case, the shapes are triangles. In the nth convex polygon, g is n and h is the sum of sides n and diagonal lines d. Therefore

$$n - (n + d) + v = 1 \qquad \text{(Eq A1.2)}$$

Then

$$-d + v = 1 \qquad \text{(Eq A1.3)}$$

Each face has three edges, which are counted twice when they are diagonal lines and once when they are sides. Therefore,

$$3v = 2d + n \qquad \text{(Eq A1.4)}$$

Then

$$v = n - 2 \qquad \text{(Eq A1.5)}$$

and

$$d = n - 3 \qquad \text{(Eq A1.6)}$$

v corresponds to the number of triangles in the polygon.

Appendix 2. Number of Triangles in a Triangulated Polygon with Points Inside

Furuta showed the extension of the above discussion to the triangulation of an nth convex polygon with m of points inside [1997Fur]. As the number of points is $(n + m)$:

$$(n + m) - (n + d) + v = 1 \quad \text{(Eq A2.1)}$$

Then

$$m - d + v = 1 \quad \text{(Eq A2.2)}$$

From Eq A1.4, we can obtain the results:

$$v = 2m + n - 2 \quad \text{(Eq A2.3)}$$

and

$$d = 3m + n - 3 \quad \text{(Eq A2.4)}$$

Appendix 3. Systematic Method for Generating All Hypothetical Reaction Schemes in the Form of the Adjacency Matrix *R*

A3.1 Concept of Nonoriented Graph for the Enumeration of Triangulated Polygons

In the text, an adjacency matrix R of $[(4n - 5) \times (4n - 5)]$ is filled with $(4n - 6)$ of numeral 1, and the rest are all numeral 0 to represent a certain reaction scheme. It was also shown that all hypothetical reaction schemes can be provided by filling each of the a_{ij} by $(4n - 6)$ of numeral 1. In this section, a practical method based on a concept on nonoriented graph is described.

Figure A3-1 shows the nonoriented form of the reaction scheme in Fig. 2. Each of the edges has no orientation, and the relationship between vertices can be described by a matrix called an adjacency matrix M, an expression similar to that for an oriented graph. It is also a square array with elements assigned numeral 0 or numeral 1, in which $a_{ij} = 1$ defines that vertex i is connected to vertex j by one edge, while $a_{ij} = 0$ does that vertices i and j have no common edge connecting each other. As $a_{ij} = a_{ji}$, the adjacency matrix M is a symmetric matrix for a nonoriented graph. This form of matrix is used to represent interconnected vertices in a triangulated nth polygon. As discussed in Appendices 1 and 2, the number of sides, diagonal lines, and triangles for any kind of triangulated nth polygon are n, $(n - 3)$, and $(n - 2)$, respectively. Therefore, the number of vertices is always $(4n - 5)$ for any kind of nth polygon.

To describe the relation among $(4n - 5)$ vertices, an adjacency matrix M of $[(4n - 5) \times (4n - 5)]$ for a nonoriented graph should be considered. Let the vertices No. 1 to n correspond to binary invariant reactions, No. $(n + 1)$ to $(3n - 3)$ to pseudobinary invariant reactions, and No. $(3n - 2)$ to $(4n - 5)$ to ternary invariant reactions in the numerical order. As all of the pseudobinary invariant reactions are connected to two of the end of edges, the number of edges is twice as many as that of pseudobinary invariant reactions. Therefore, this relationship can be treated as a graph with $(4n - 5)$ vertices connected by $2 \times (n + n - 3) = (4n - 6)$ edges. The connections between two vertices corresponding to ternary invariant reactions through a vertex corresponding to a pseudobinary invariant reaction represent a construction of a polygon from triangles. Thus, the enumeration of all kinds of nonoriented graph means the enumeration of all kinds of triangulated patterns of a certain polygon.

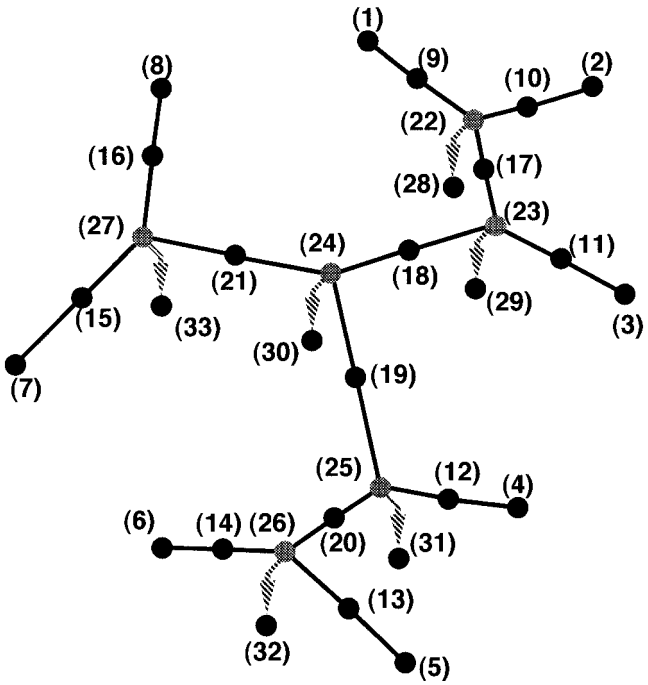

Fig. A3.1 Network of flow lines and vertices, which correspond to ternary, binary, and pseudobinary invariant reactions expressed without the information on invariant reaction temperatures

The interconnection of vertices in a triangulated ternary phase diagram is described in a form of an adjacency matrix M as follows: Each of the vertices No. 1 to n is an endpoint of only one edge connected with one of the vertices No. $(n + 1)$ to $2n$, i.e., pseudobinary invariant reactions. Similarly, the vertices No. $(2n + 1)$ to $(3n - 3)$ are the endpoint of two edges connected with vertices No. $(3n - 2)$ to $(4n - 5)$, and vertices No. $(3n - 2)$ to No. $(4n - 5)$ are that of three edges connected with vertices No. $(n + 1)$ to No. $(3n-3)$. Because an adjacency matrix M for a nonoriented graph is symmetric, one should take only submatrices A, B, and C into account for the representation and enumeration, as shown in Fig. A3-2, where ${}^tA$, ${}^tB$, and ${}^tC$ are transpositions of submatrices A, B, and C, respectively. Figure A3-2 shows a matrix M for a nonoriented graph shown in Fig. A3-1. Submatrix A represents the relations between the vertices No. 1 to n (No. 8 in Fig. A3-2) and the vertices No. $(n + 1)$ (No. 9 in Fig. A3-2) to No. $(2n)$ (No. 16 in Fig. A3-2). Submatrix B represents the relations between the vertices No. $(n + 1)$ (No. 9 in Fig. A3-2) to No. $(2n)$ (No. 16 in Fig.

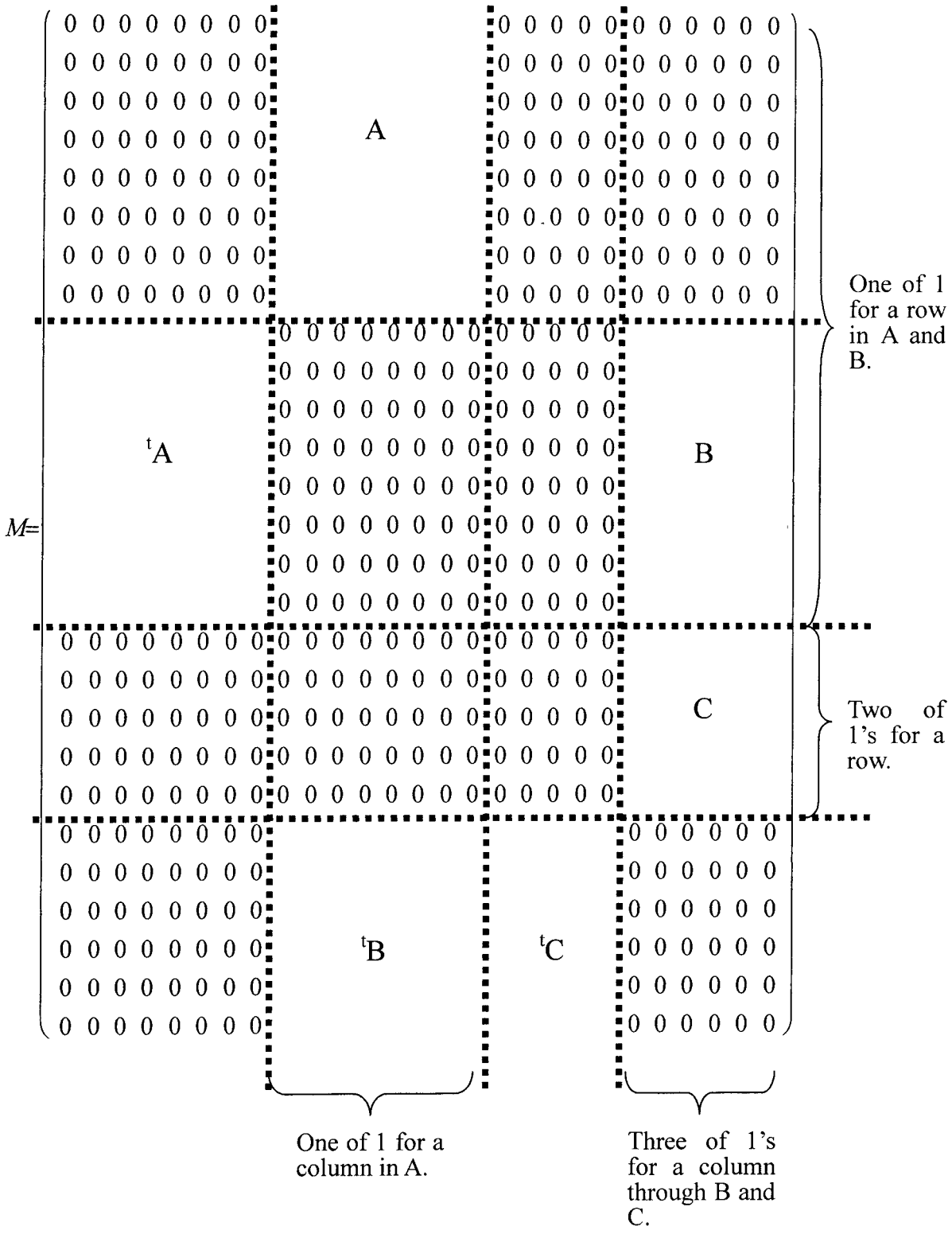

Fig. A3.2 Adjacency matrix expression of the reaction scheme in the form of the nonoriented graph

A3-2) and the vertices No. ($3n - 2$) (No. 22 in Fig. A3-2) to No. ($4n - 5$) (No. 27 in Fig. A3-2). Submatrix *C* represents the relations between the vertices No. ($2n + 1$) (No. 17 in Fig. A3-2) to No. ($3n - 3$) (No. 21 in Fig. A3-2) and the vertices No. ($3n - 2$) (No. 22 in Fig. A3-2) to No. ($4n - 5$) (No. 27 in Fig. A3-2)—in other words, relations between diagonal lines and triangles. In this treatment, each row of the submatrices *A* and *B* must have one numeral 1 element

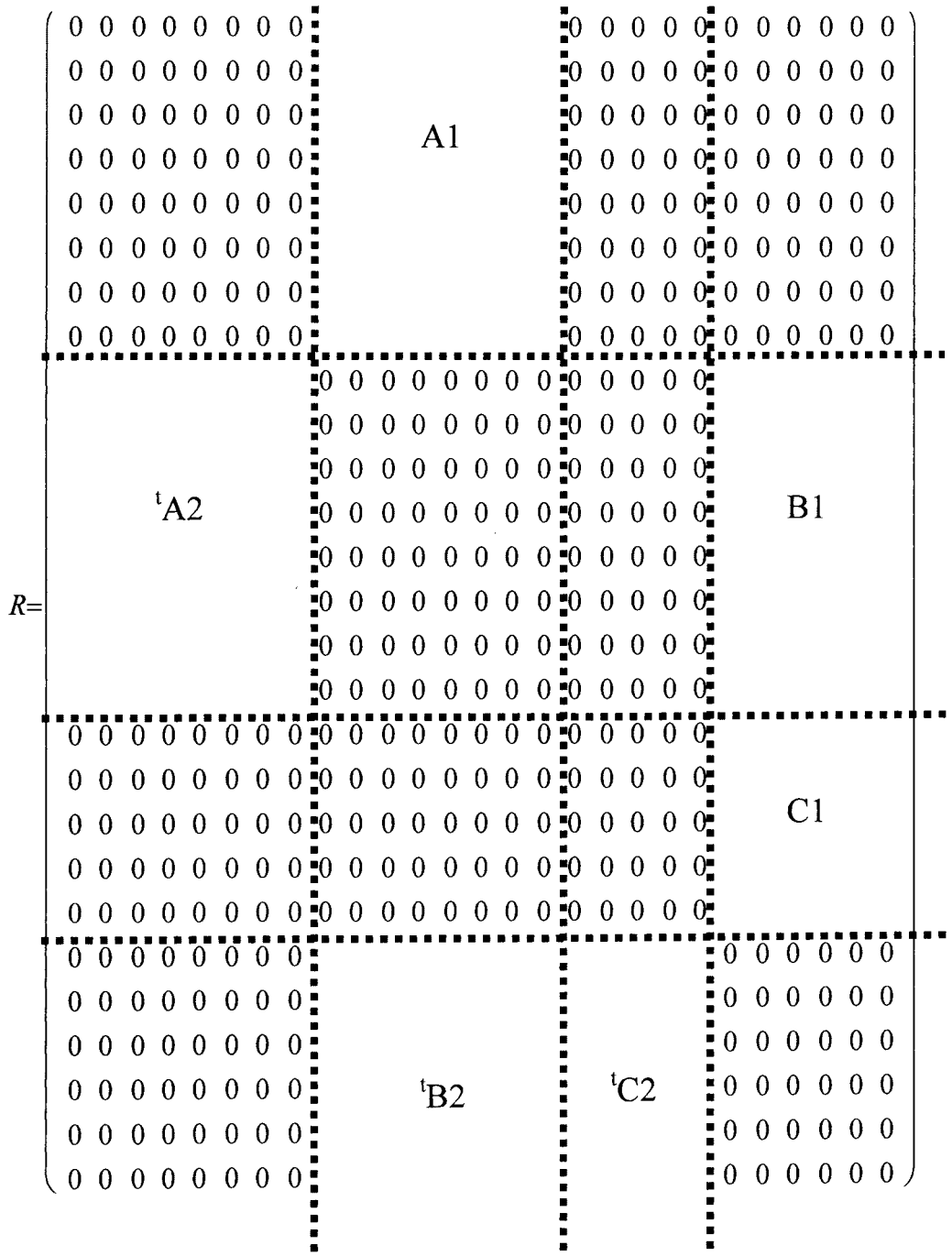

Fig. A3.3 Adjacency matrix expression of the reaction scheme in the form of the oriented graph

and the other elements left must all be numeral 0. Similarly two numeral 1s appear in each row of the submatrix *C*, which represents each of diagonal lines is connected to two of triangles. Besides, the number of the numeral 1 appearing in each column of submatrix *A* must be one. Moreover, the number of the numeral 1 appearing in each column through submatrices *B* and *C* must be three, which represents each of the ternary invariant reactions, is connected to pseudobinary invariant reactions by three edges. It can be seen that this configuration is generated from only the rule of connection of monovariant lines in a ternary phase diagram without the information on invariant reaction temperatures. It can be easily pointed out that, by enumerating all patterns of the submatrices *A*, *B*, and *C* with the rule mentioned, every neighboring pattern of vertices that corresponds to each triangulated pattern of a certain ternary phase diagram can be enumerated. To avoid double counting and exclude equivalents, the filling in the entries in the submatrices *A*, *B*, and *C* with numerals 1 and 0 must be carried out in a systematic manner.

A3-2. Generation of Oriented Graphs from a Non-oriented Graph

The reaction scheme presents the relation among invariant reaction temperatures by oriented lines connected at two invariant reactions to show which reaction occurs at a higher temperature. To model the reaction scheme consistently with information on reaction temperatures, the concept of an oriented graph was introduced in the text.

Here a method is described to derive all candidates for the reaction scheme in the form of the oriented graph. The nonoriented graph represents only a neighboring pattern of vertices concerning to a certain triangulation pattern of an *n*th polygon. By orienting each edge of a corresponding nonoriented graph individually, all candidates will be produced. In the adjacency matrix M for a non-oriented graph, $a_{ij} = a_{ji}$, and the adjacency matrix M is a symmetrical matrix. The orienting of edges means to select either $a_{ij} = 1$ or $a_{ji} = 1$ in the adjacency matrix R for an oriented graph. Mathematically, the orienting of a non-oriented graph can be done by dividing submatrices A, B, and C into two parts consisting of numerals 1 and/or 0 individually:

$$A = A1 + A2 \quad \text{(Eq A3.1)}$$

$$B = B1 + B2 \quad \text{(Eq A3.2)}$$

and

$$C = C1 + C2 \quad \text{(Eq A3.3)}$$

In this case, ${}^{t}A2$, ${}^{t}B2$, and ${}^{t}C2$, which are transpositions of newly introduced submatrices $A2$, $B2$, and $C2$, respectively, are used instead of ${}^{t}A$, ${}^{t}B$, and ${}^{t}C$, as shown in Fig. A3-3. This mathematical treatment provides all candidates for the reaction scheme, which is referred to as a "hypothetical" reaction scheme, in the form of an adjacency matrix R for a certain oriented graph.

Let us summarize the enumeration method for hypothetical reaction schemes. It involves two steps. In the first step, submatrices A, B, and C in a form of nonoriented graph are derived for the enumeration of the triangulation patterns. Then in the second step, $A1$, $A2$, $B1$, $B2$, $C1$, and $C2$ are derived from A, B, and C. Note that in each of the above steps, the same process must be repeated until all the submatrices can be obtained for further inspection. This iterative nature of the method allows a computer to be programmed to provide all hypothetical reaction schemes.

References

1966Pri: A. Prince, *Alloy Phase Equilibria,* Elsevier Publishing Company, Amsterdam, The Netherlands, 1966

1967Kau: A. Kaufmann, *Graphs, Dynamic Programming, and Finite Games,* H.C. Sneyd, trans., Academic Press, New York, 1967

1972Gar: R.S. Garfinkel and G.L. Nemhauser, *Integer Programming,* John Wiley & Sons, New York, 1972

1983Pol: G. Pólya, R.E. Tarjan, and D.R. Woods, Notes on Introductory Combinatorics, Birkhäuser Boston, Boston, MA, 1983.

1994Con: R.G. Connell, Jr., A Tutorial on Flow Diagrams: A Tool for Developing the Structure of Multicomponent Phase Diagrams, *J. Phase Equilibria,* 1994, 15, p 6

1995Vil: P. Villars, A. Prince, and H. Okamoto, *Handbook of Ternary Alloy Phase Diagrams,* ASM International, 1995

1997Fur: A. Furuta, Polygon and Combination, *Basic Mathematics,* 1997, 30 (6), p 33, in Japanese

1999Slu: E.M. Slyusarenko, V.A. Borisov, M.V. Sofin, E.Yu. Kerimov, and A.E. Chastukhin, Determination of Phase Equilibria in the System Ni-V-Cr-Mo-Re at 1425 K Using the Graph Method, *J. Alloys Compd.,* 1999, 284, p 171

2001Miu: S. Miura, H. Unno, T. Yamazaki, S. Takizawa, and T. Mohri, Reinvestigation of Ni-Solid Solution/Liquid Equilibria in Ni-Al Binary and Ni-Al-Zr Ternary Systems, *J. Phase Equilibria,* 2001, 22, p 457

2001Sof: M.V. Sofin, E.Yu. Kerimov, A.E. Chastukhin, N.A. Bazhanova, Yu.V. Balykova, and E.M. Slyusarenko, Determination of Phase Equilibria in the Ni-V-Nb-Ta-Cr-Mo-W System at 1375 K Using the Graph Method, *J. Alloys Compd.,* 2001, 321, p 102