

## **Application of thermodynamics, phase equilibria and kinetics to *in-situ* composite synthesis via ternary solid-state displacement reactions**

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**Abstract:** High-temperature structural composites being developed today use matrix materials and reinforcing fibers which are rarely at thermodynamic equilibrium. The use of coatings to protect the fibers from deteriorating reactions at the interface adds processing and manufacturing costs. If structural composites are going to be synthesized competitively, we must find *in-situ* processes that can produce thermodynamically stable interfaces between the matrix and the reinforcement. One such process which is being developed to synthesize structural composites is via a ternary solid-state displacement reaction.

In the present paper, the thermodynamic and kinetic conditions governing the formation of desirable microstructure for structural composites via the solid-state displacement reaction are formulated. They are applied to a ternary silicon-metal-carbon system for possible synthesizing a metal silicide-silicon carbide composite.

### Introduction

Composite materials, whether they are metal-matrix, ceramic-matrix or intermetallic-matrix, offer the potential to be the next generation of materials for applications at high temperatures. Most of these composites being developed use matrix materials and reinforcing fibers which are rarely in thermodynamic equilibrium with each other. This means the fibers need to be coated with one or more materials which must be chemically and mechanically compatible with the fibers and matrix materials. Even if suitable coatings are developed, there is an added cost in the processing and manufacturing of this type of composites. Moreover, the coatings must be perfect in order to protect the fibers from interaction with the matrix materials. Any local degradation between the coating and the fibers would destroy the mechanical properties of the composite. While this approach to making structural composites should be continued, we must also look into the future to develop a knowledge base for making structural composites by *in-situ* processes. The component elements made in such a composite via an *in-situ* process are certainly at thermodynamic equilibrium/or metastable thermodynamic equilibrium such as the formation of ferrite and cementite from the eutectoid decomposition of austenite.

Due to their high strength, high melting point and oxidation resistance, some transition metal silicides, i.e., compounds consisting of a transition metal and silicon, as well as composites using these silicides as the matrix materials, have been explored as potential high-temperature materials. In fact, Henager et al. (1) have attempted recently to synthesize a  $\text{MoSi}_2/\text{SiC}$  composite *in-situ* using a solid-state displacement reaction between  $\text{Mo}_2\text{C}$  and Si. This type of displacement reaction may offer a potential route for making high-temperature structural composites via an *in-situ* process. However, several different microstructures can be produced from a ternary solid-state displacement reaction. Not all of the microstructures produced are suitable for good structural composites. In order to be able to predict or even control the type of microstructure formed from a combination of the reacting component elements, we must know the growth mechanisms for a specific class of composite system. The phase relationships of the pertinent ternary systems and the diffusion data of the component elements in the

phases formed from the reacting components are the two fundamental data required to establish the growth mechanisms.

Rapp and co-workers (2-4) were the first to study the formation of two types of microstructures from such a displacement reaction. They named these two types of microstructures layered and aggregate structures. The formation of a  $\text{MoSi}_2/\text{SiC}$  composite from  $\text{Mo}_2\text{C}$  and Si as investigated by Henager et al. (1) might correspond to the conditions for the formation of the aggregate structure. The arguments for rationalizing the occurrence of these two types of microstructures were given by Wagner (5,6) and demonstrated experimentally and theoretically by Rapp and co-workers (2-4) using oxidation/reduction reactions. Their studies demonstrate that if we have the thermodynamic description and the phase equilibria of the ternary system in question, as well as diffusion data of the component elements in the various phases, we can predict the type of microstructure, i.e., the layered or aggregate type, which may form in a specific ternary diffusion couple via a displacement reaction. However, other types of microstructures may also result from a solid-state displacement reaction, as is discussed below.

In addition to the two types of microstructures mentioned above, a third type of microstructure, a periodic layered structure, has been reported to form in some ternary diffusion couples also involving a solid-state displacement reaction, such as  $\text{Fe}_3\text{Si}/\text{Zn}$  (7),  $\text{Co}_2\text{Si}/\text{Zn}$  (7,8),  $\text{SiC}/\text{Ni}$  (7,8),  $\text{CoNi}/\text{Mg}$  (9),  $\text{SiC}/\text{Pt}$  (10) and  $\text{GaAs}/\text{Co}$  (11). Even though this type of microstructure was first discovered in 1982 (7), a thermodynamic and kinetic description for the formation of this microstructure was not offered until the recent work of Kao and Chang (12). Van Loo and co-workers (8) made the speculation that the formation of a periodic layered structure is due to the creation of stresses at the interfaces. However, there is not any experimental evidence to support this speculation.

Kao and Chang (12,13) presented a thermodynamic argument for the formation of this type of microstructure via a solid-state displacement reaction. Moreover, they formulated a diffusion model which accounts semi-quantitatively for the formation of this periodic layered structure. According to their model, formation of this structure is due to the thermodynamics/phase relationships of the ternary system and the diffusivities of the component elements. The condition for the formation of this structure is that the diffusivity of one of the component elements within the diffusion zone is much higher than that of the other component elements. Again, if we know the thermodynamics/phase relationships of the ternary system and diffusion data we can forecast what combinations of the two reactants which may produce this type of microstructure.

The objectives of this paper are (i) to present the thermodynamic and kinetic conditions for the formation of the three types of microstructures via a solid-state displacement reaction and (ii) to apply these principles to the study of reacting  $\text{Si}/\text{M}_\delta\text{C}$  as a means of making structural composites of  $\text{MSi}_2/\text{SiC}$ . The symbol M denotes one of the groups IVA, VA and VIA transition metals and  $\delta$  is a stoichiometric coefficient.

### Thermodynamic Considerations

If we wish to make a composite consisting of a matrix component with reinforcing fibers, we would use a pair of component elements which are not at thermodynamic equilibrium. These two component elements will react with each other, forming a composite consisting of the matrix and reinforcing fibers with the desired microstructure. The extent of interaction and the resulting microstructure from these two component elements are governed by the thermodynamics/phase equilibria and the kinetics of the ternary system under consideration. This means we must first understand the phase relationships and thermodynamics of the ternary system and then the kinetics of the reacting phases. Let us discuss the thermodynamic and kinetic issues of a ternary system exhibiting a schematic phase diagram shown in Fig. 1.

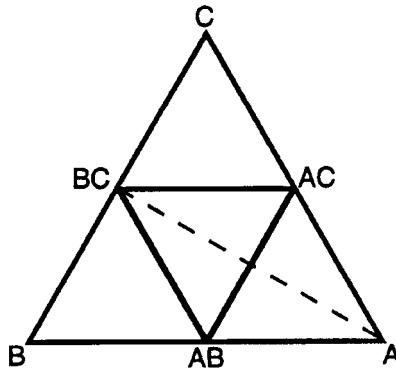


Fig. 1 A hypothetical phase diagram of A-B-C with the three intermediate phases AB, AC and BC in equilibrium with each other.

Suppose we wish to make a composite consisting of AB/AC, we can start with the combination of BC and A. Since BC and A are not at thermodynamic equilibrium, a reaction will occur at the BC/A interface, resulting in the formation of AB/AC. In the following we will first introduce the concept of diffusion path and then the kinetic principles governing the type of microstructure formed from a combination of BC/A to yield a composite of AB/AC.

#### Kinetic Considerations

Thermodynamics determines what phases can coexist when equilibrium conditions are achieved, but does not determine what combinations of phases which may form in the process of achieving equilibrium. For instance, from the phase diagram given in Fig. 1, it cannot be predicted which reaction product phases will form prior to achieving equilibrium when BC is in contact with A. While only one diffusion path is possible in a binary diffusion couple, this is not true for ternary or higher order couples. A diffusion path represents a specific arrangement of phases in a diffusion couple under steady state conditions, in which each phase is in thermodynamic equilibrium with its neighboring phases. If A is placed in contact with B as shown in Fig. 1, the intermediate phase AB will form in the sequence A|AB|B; this is the only diffusion path possible for this binary system. On the other hand, if A is placed in contact with BC, there is more than one possible diffusion path. The two most likely possible diffusion paths are BC|AC|AB|A and BC|AB|AC|A. However, when C is relatively immobile, the preferred path would be BC|AC|AB|A. The condition that the component C is relatively immobile has frequently been found to be the case in ternary systems (14). Now we will present the conditions which favor the formation of either a layered structure, i.e. BC|AC|AB|A, or an aggregate structure, i.e. BC|AC+AB|A, based on the idealized diffusion and reaction mechanism presented below.

Figure 2(a) shows the layered arrangement of BC|AC|AB|A. The component A diffuses through the layers AB and AC to react with BC at the BC/AC interface to form AC. The chemical reaction at this interface as shown in Fig. 2(a) is



The component element B formed from this reaction then diffuses through the layer AC to react with A, which diffuses through the layer AB, to form AB at the AC/AB interface according to the following reaction:



The criteria used to determine the interfacial stability were first formulated by Wagner (5,6) and were subsequently applied successfully by numerous others (2-4,11,14-19) to solid-state diffusion systems. The stability of an interface is determined by the direction of the growth front of a particular phase in

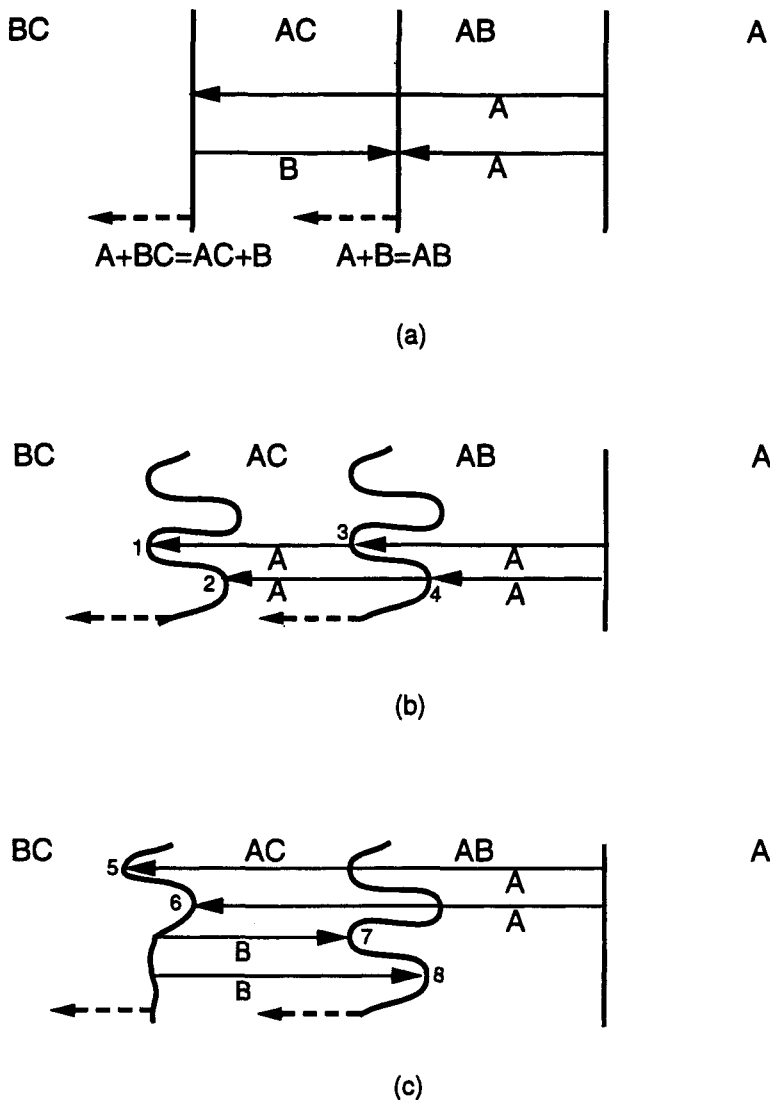


Fig. 2 Interfacial Stabilities of BC/AC and AC/AB in a ternary diffusion couple of BC/A.

question and the rate controlling diffusing species. In the system shown in Figs. 1 and 2(a), the growth front of the layer AC is toward left, since A reacts with BC to form AC at the BC/AC interface. The growth front of the layer AB is also toward the left since it grows at the AC/AB interface.

#### Formation of a Layered Structure

Let us consider the BC/AC interface first. The rate-limiting step for the reaction at this interface is the rate at which the A atoms reach this interface. Suppose a perturbation occurs at the BC/AC interface. As shown in Fig. 2(b), the component A diffuses to point 2 faster than point 1. This means that the growth front at point 2 grows faster than that at point 1, thus stabilizing the planar interface between BC and AC.

Let us next examine what may happen at the AC/AB interface. In order to answer this question, we must know whether the diffusion of B to the interface is the rate limiting step or that of A is the rate limiting step. If the diffusion of A through AB is slower than that of B through AC, then the diffusion

of A through AB is the rate limiting step. As shown in Fig. 2(b), A arrives at point 4 much sooner than at point 3, stabilizing the AC/AB interface. Thus, we would have a layered structure, since both of the interfaces where reactions occur are stabilized.

#### Formation of an Aggregate Structure

On the other hand, if diffusion of B through AC is slower than that of A through AB, the rate limiting step is the diffusion of B through AC, as shown in Fig. 2(c). The component B reaches point 7 sooner than point 8. This means the interface at point 7 grows faster than at point 8, causing instability at the AC/AB interface, resulting in the formation of an aggregate structure. As pointed out originally by Wagner (5,6) the condition shown in Fig. 2(c) may lead to interfacial stability but does not assure that instability will occur. The interface at BC/AC is again planar as discussed earlier. In other words, the component A reaches point 6 sooner than point 5; thus stabilizing the BC/AC interface.

The conditions for the formation of the layered (planar) and aggregate structures as shown in Fig. 2 are summarized in Table 1. It is noteworthy to point out that Rapp and co-workers (2-4) and Chang and co-workers (18-20) have applied the criteria formulated by Wagner (5,6) quite successfully to numerous ternary solid-state diffusion couples.

TABLE 1  
The Conditions for Interfacial Stability of a Ternary Diffusion Couple  
BC/A With the Phase Equilibria Shown in Fig. 1

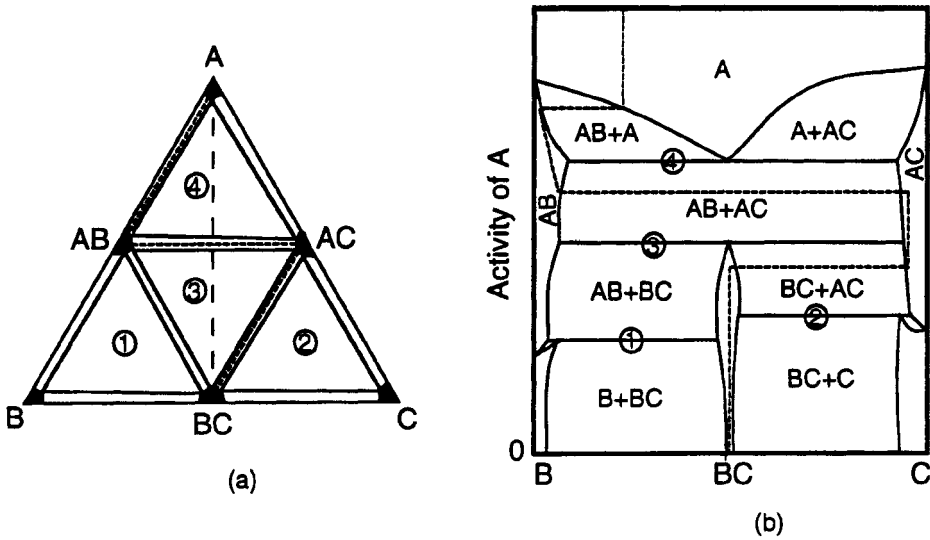
	Conditions*	Resulting Microstructure of AB/A
I	$D_A(AB) < D_B(AC)$	Layered Structure
II	$D_A(AB) > D_B(AC)$	Aggregate Structure
III	$D_A(AB) \gg D_B(AC)$	Periodic Layered Structure

\* $D_i(\alpha)$  denotes the diffusion coefficient of component  $i$  in the phase  $\alpha$ . Since the interfacial stability is controlled by the relative fluxes of the diffusing species, the conditions given in this table are true in most cases.

#### Formation of a Periodic Layered Structure

Next we wish to discuss the conditions under which a periodic layered structure may form in a ternary diffusion couple of BC/A, as given in Fig. 1. (12,13) In order to present the ideas in a clear manner, we must also have a stability diagram in terms of the activity of A, i.e.,  $a_A$ , in addition to the phase diagram shown in Fig. 1. This is necessary, since the driving force for diffusion of a component element is its chemical potential gradient. Figure 1 is reproduced in Fig. 3(a). In this figure, all the phases are drawn with noticeable solubilities, and the component A has been placed at the top of the Gibbs triangle for ease of visualization. Figure 3(b) shows the  $a_A$  in terms of the mole fraction of C in (B+C), i.e.,  $y_C = n_C/(n_B+n_C)$ , where  $n_i$  denotes the moles of B and C.

The diffusion path for the formation of a simple layered structure, is drawn in Fig. 3(a) and 3(c) as A|AB|AC|BC. However, we cannot tell from either Fig. 3(a) or Fig. 3(c) how  $a_A$  varies across the diffusion couple. A diffusion path is drawn in the stability diagram in Fig. 3(b). The activities of A across all the two-phase fields remain constant. Remember that the condition for the formation of a layered structure is  $D_A(AB) < D_B(AC)$  and of an aggregate structure is  $D_A(AB) > D_B(AC)$ . Let us examine the case when  $D_A(AB) \gg D_B(AC)$ . Under such a condition, the supply of B at the AB/AC interface is insufficient to react with all the A atoms at this interface to form AB. As a result, there is an accumulation of A atoms at the BC/AC interface. Let us now examine the range of  $a_A$  (referring to Fig. 3(b)) under which the phase BC is thermodynamically stable. When  $a_A$  is greater than  $a_{A\ominus}$ , corresponding to the  $a_A$  for the AB+BC+AC three-phase equilibrium, the phase BC becomes thermodynamically unstable. With continual accumulation of A at the BC/AC interfaces,  $a_A$  increases. When it is greater than  $a_{A\oplus}$ , BC becomes unstable. The phase AB then forms and grows, provided nucleation is not a problem. The formation of AB causes the formation of AC. The process repeats itself to produce the periodic layered structure as shown in Fig. 3(d). Kao and Chang (12,13) also



The numerals ①, ②, ③, and ④ in the above two figures refer to the same three-phase equilibria; the dashed line - - - connects the end members of the diffusion couple, and the dashed lines ——— represent the diffusion path.

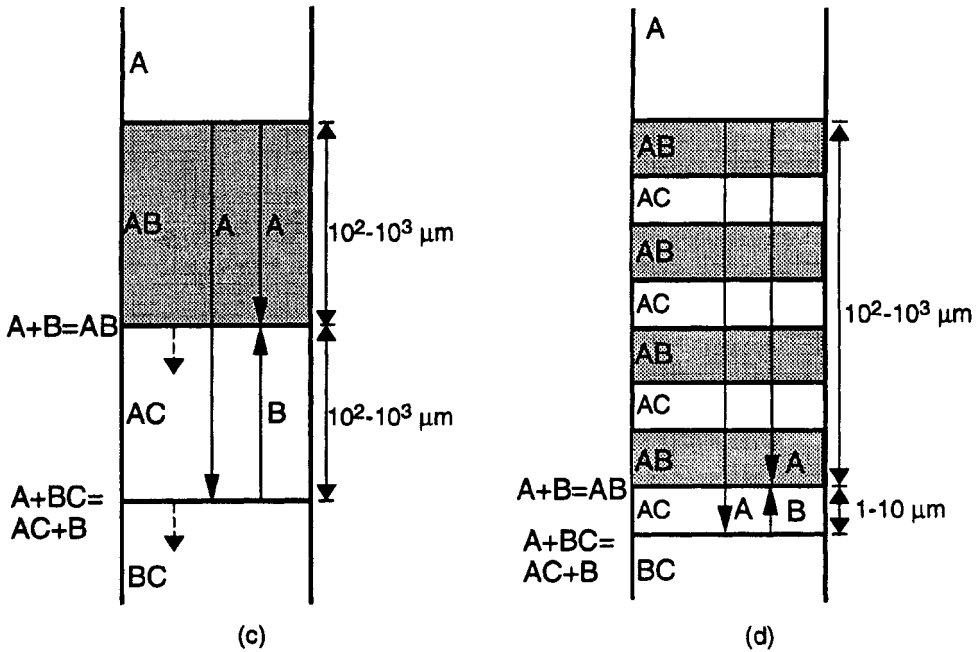


Fig. 3 Two types of phase diagrams of a hypothetical A-B-C system and the arrangements of the layered and periodic layered structures formed from a diffusion couple of BC/A.

formulated a kinetic model to account semi-quantitatively for the formation of the periodic structure. The model is semi-quantitative because simplifying but reasonable assumptions had to be made in order to obtain a solution from the differential equations in a close-form. The numerical results of the kinetic model show the ratio of  $D_A(AB)/D_B(AC)$  is the dominant factor in governing the formation of the periodic layered structure.

A comparison of Figs. 3(c) and 3(d) shows the arguments presented above are quite reasonable for the formation of the two types of structure. When  $D_A(AB)$  and  $D_B(AC)$  are comparable in magnitude, they both diffuse over a distance of  $10^2$ - $10^3$   $\mu\text{m}$  when a layered structure is formed. On the other hand, when  $D_A(AB) \gg D_B(AC)$ , A diffuses over a distance of  $10^2$ - $10^3$   $\mu\text{m}$  while B only diffuses 1-10  $\mu\text{m}$  when a periodic layered structure is formed. The conditions for the formation of the periodic layered structure are also summarized in Table 1.

It is evident from the presentation on the formation of the three types of microstructure from a combination of BC/A via a solid-state displacement reaction that if we know the thermodynamics of the ternary A-B-C system and the diffusion data, we are in a position to predict the type of microstructure of BC/AC which may form from BC/A. The desirable microstructure for synthesizing a structural composite via the displacement reaction is the aggregate type. In the next section we will first review the phase relationships of nine Si-M-C systems. In light of the theoretical discussion given earlier and the Si-M-C phase relationships, we will discuss the likelihood of synthesizing structural composites of  $\text{MSi}_2/\text{SiC}$  using this type of solid-state displacement reaction. Moreover, we will discuss the type of fundamental research needed to be carried out in order to provide a better understanding of this type of reactions.

#### Phase Relationships of Si-M-C and the Synthesis of $\text{MSi}_2/\text{SiC}$ Composites

Figure 4 shows schematically the isothermal sections of nine Si-M-C systems. The references from which these diagrams were taken are given below: Si-Ti(Zr,Hf)-C (21), Si-V-C (22), Si-Nb-C (23), Si-Ta-C (24), Si-Cr-C (25), Si-Mo-C (25) and Si-W-C (21). Van Loo et al. (26) reported phase equilibria of Si-Mo-C which differ from those shown in Fig. 4. However, a recent investigation by Costa e Silva and Kaufman (27) demonstrated that the diagram determined by Nowotny et al. (25), shown in Fig. 4, is correct. In the original work of Nowotny et al. (25) MoC was thought to be stable at 1600°C. However, a more recent investigation (21) showed that MoC is not stable, and it is not known in Fig. 4. In all of these diagrams, the ranges of homogeneity of most of the phases are neglected, since we wish to show only the general topology of the phase equilibria. The monocarbides of the IVA and VA metals (with the exception of TaC) are shown with their ranges of homogeneity. More recent studies related to the phase equilibria of Si-Ti-C include the works of Wakelkamp et al. (28), Choi et al. (29), Gottselig et al. (30) and Morozumi et al. (31).

As shown in Fig. 4,  $\text{MSi}_2$  is in equilibrium with SiC, and a three phase equilibrium of  $\text{Si-M}_3\text{C-SiC}$  exists in all the cases except for Si-Ti-C, Si-Cr-C and Si-Mo-C. Other than Si-V-C and Si-W-C, a ternary phase exists in all the systems. Since the phase equilibria of Si-V-C were estimated on the basis of the thermodynamic data of the binary phases, a ternary phase may indeed also exist in this system.

Although the phase relationships of the nine Si-M-C systems shown in Fig. 4 are more complex than those of the model system given in Fig. 1, the basic principles may be used to assess whether a reaction of Si with one of the binary (or ternary) carbide phases may be used to make a structural composite via a solid-state displacement reaction. Let us now take the Si-Nb-C ternary system as example for discussion. The 1300°C isotherm given in Fig. 4 shows SiC and  $\text{NbSi}_2$  are in thermodynamic equilibrium. This means the possibility does exist that Si may react with NbC to form an aggregate type of structure of  $\text{NbSi}_2/\text{SiC}$ . An examination of the phase relationships of Si-Nb-C shows that numerous diffusion paths are possible between Si and NbC. However, by analyzing the thermodynamics of this system, we have eliminated most of the impossible paths (32). The two possible paths left are NbC|SiC| $\text{NbSi}_2$ |Si and NbC| $\text{NbSi}_2$ |SiC|Si. The question remains is whether the SiC| $\text{NbSi}_2$  and  $\text{NbSi}_2$ |SiC interfaces are stable to form planar interfaces or unstable to form an aggregate-type of structure, desirable for structural composites. An analysis of the situation is given in Fig. 5.

Figure 5(a) shows a possible mechanism for the growth of SiC and  $\text{NbSi}_2$  in a couple of NbC/Si. Silicon diffuses through the layers of  $\text{NbSi}_2$  and SiC to react with NbC at the NbC/SiC interface to form SiC and Nb. The Nb released from this reaction diffuses through the SiC layer to react with Si at the SiC/ $\text{NbSi}_2$  interface to form  $\text{NbSi}_2$ . As Fig. 5(a) shows, the NbC/SiC is always planar since the growth front of SiC into NbC is in the same direction as that of Si diffusion. Whether the SiC/ $\text{NbSi}_2$

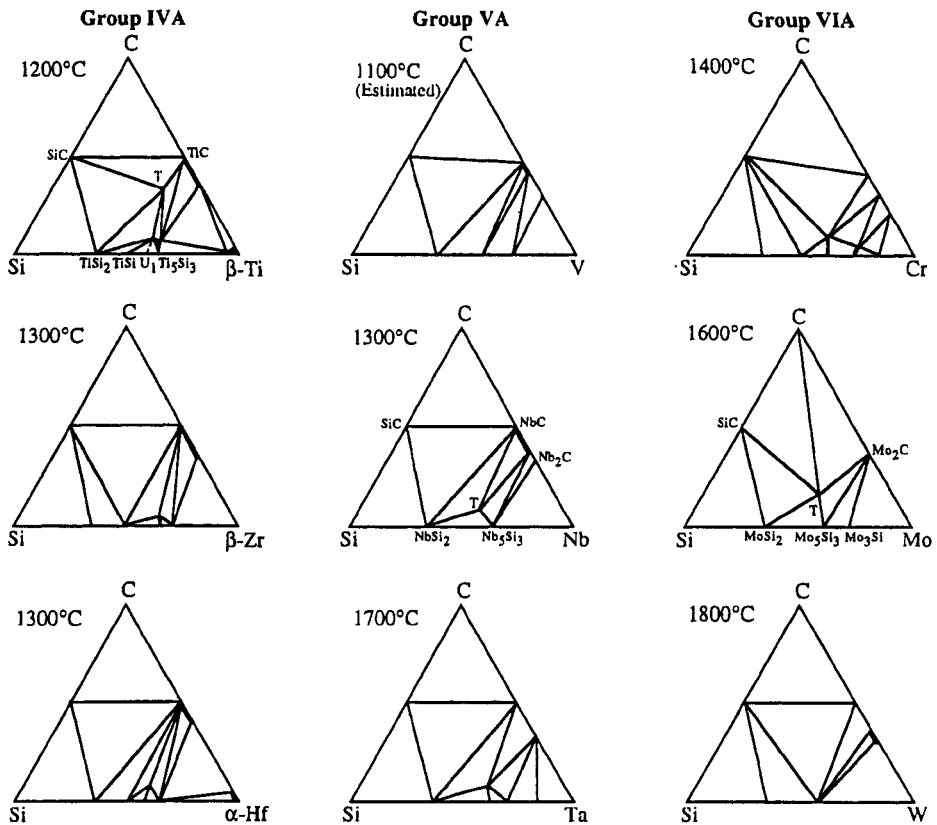


Fig. 4 Phase diagrams of nine Si-M-C systems.

interface is stable or not depends on the relative fluxes of Nb in the SiC layer versus that of Si in the NbSi<sub>2</sub> layer. If the diffusivity of Nb in SiC is slower than that of Si in NbSi<sub>2</sub>, then the SiC/NbSi<sub>2</sub> interface is unstable, resulting in an aggregate-type structure. A similar analysis for the structure given in Fig. 5(b) shows that an aggregate structure of NbSi<sub>2</sub>/SiC would also form if the diffusivity of C in NbSi<sub>2</sub> is smaller than that of Si in SiC. Although no diffusion data were found in the literature, the study of Henager et al. (1) in synthesizing a MoSi<sub>2</sub>/SiC composite indicates that Si is a fast diffuser. If this is indeed the case, we would expect that there is an excellent possibility that a composite of NbSi<sub>2</sub>/SiC may be made by reacting Si with NbC.

We are currently carrying out Si/NbC diffusion couple experiments in our laboratory. The results of the experiments will be correlated with the theoretical analysis. In addition, we plan to carry out more diffusion-couple experiments using other combinations of end phases with the objective of understanding the diffusional behavior of Si-Nb-C and hopefully for the Si-M-C systems.

### Conclusion

It has been shown that the principles of thermodynamics, phase equilibria and kinetics of multi-component systems can be used effectively in the design of solid-state reactions for synthesizing structural composites. In the present study, we have focused on the synthesis of MSi<sub>2</sub>/SiC composites via solid-state displacement reactions. However, in order to be able to apply these principles for technological applications, it is essential to have fundamental data and an understanding of the thermodynamics, phase equilibria and kinetics of the systems involved.



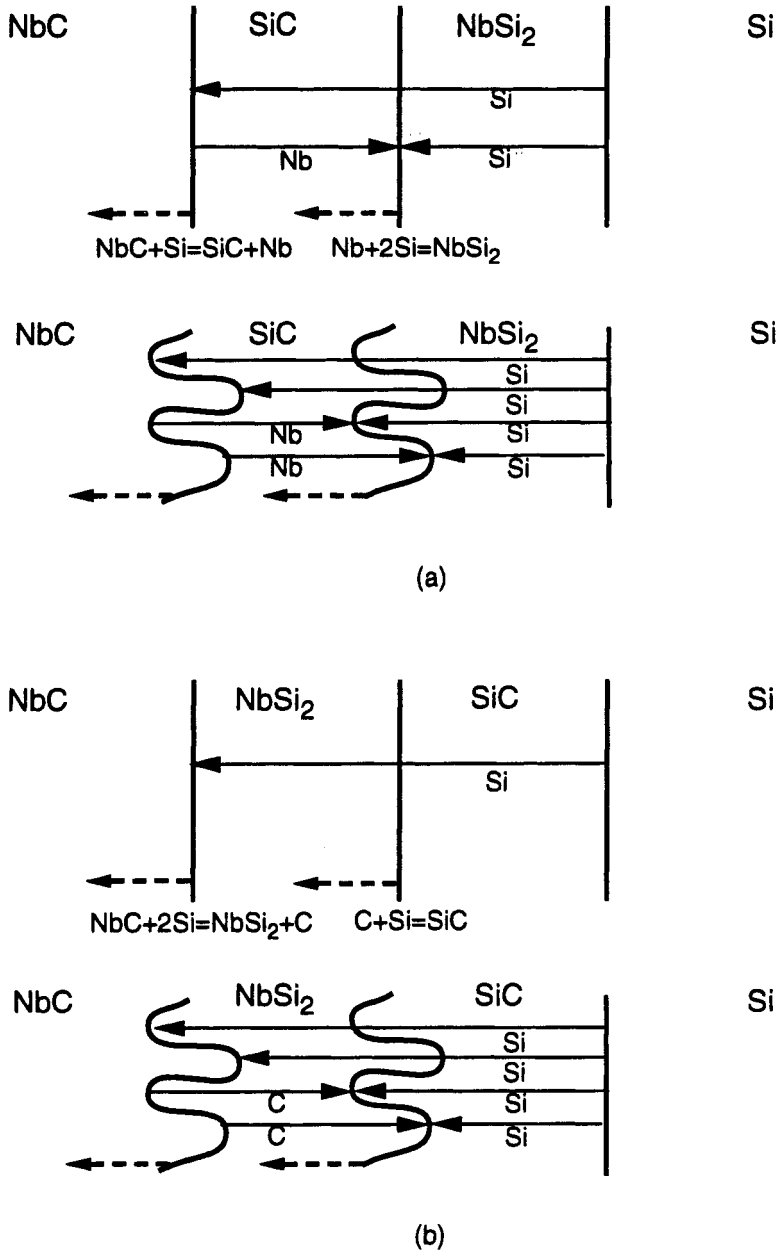


Fig. 5 The conditions for the formation of an aggregate-type structure of SiC and NbSi<sub>2</sub> in a diffusion couple of Si/NbC.

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