

## MoSi<sub>2</sub> AND OTHER SILICIDES

### AS HIGH TEMPERATURE STRUCTURAL MATERIALS

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#### Abstract

There has been a revival of interest in MoSi<sub>2</sub> and other refractory silicides, hitherto used for heating elements and coatings, as high temperature structural materials. With their high melting point and excellent high temperature oxidation resistance, silicides as a class of intermetallics, have potential for developing temperature capability beyond nickel base superalloys. Though metal like in their physical properties, silicides are in general brittle at room temperature. This drawback is being addressed through a variety of in-situ and artificial composite approaches. This paper attempts to provide a perspective on these approaches with a review of current activities. To provide a background, the development strategies for high temperature structural materials are discussed, followed by an overview on formation of silicides. The relevant mechanical and physical properties and environmental resistance of silicides are compared using superalloys as the benchmark, to help assess the risks versus benefits. Finally, the paper concludes with a brief summary of primarily fiber reinforced MoSi<sub>2</sub> composites and ductile phase reinforced in-situ composites based on other silicides. The unavailability of suitable fibers and interface coating for conventional composites and containerless solidification for in-situ composites are identified as the principal problems.

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## Introduction

Since as early as 1956, molybdenum disilicide ( $\text{MoSi}_2$ ) based material has been commercially available as Super Kanthal [1], along with nickel-chromium based heating elements. Those in the aerospace industry are also familiar with commercially available silicide coatings used for protecting refractory metal components[2]. There is considerable interest and application of silicides in the semiconductor industry as good electrical conductors and diffusion barriers in integrated circuits[3]. Thus current interest in  $\text{MoSi}_2$  and other silicides is not a newly found esoteric curiosity, but a revival with a new mission aimed at exceeding the temperature capability of the state-of-the-art single crystal superalloys.

What has sustained the current interest, is the excellent oxidation resistance of  $\text{MoSi}_2$ , but what has dampened progress is its lack of room temperature ductility and toughness. Given this background and the long history of development of superalloys, it is unlikely that the next generation of high temperature materials with a quantum jump in temperature capability will be developed tomorrow. Yet innovations cannot be predicted and the inherent melting point limitation of nickel base alloys cannot be ignored. It is in this spirit that this review of current development activities for  $\text{MoSi}_2$  and other silicides with melting point in excess of  $2900^\circ\text{F}$  ( $1600^\circ\text{C}$ ) is presented.

To provide a background the development strategies for high temperature structural materials is discussed, followed by a review of formation of silicides. The relevant mechanical and physical properties and environmental resistance of silicides, are compared using superalloys as the benchmark, to help assess the risks versus benefits. Finally the paper concludes with a brief summary of various composite processing techniques.

### Development Strategies for Structural Applications

Optimistically as depicted in Figure 1, silicides may be used as single phase monolithic materials, much the same way as  $\text{Ni}_3\text{Al}$  [5] and  $\text{NiAl}$  [6], with considerable tensile ductility in single crystal form. However, the extension of the nickel base alloy experience to many non-cubic and more covalently bonded silicides is not simple as we shall discuss further. None the less, in spite of being brittle, monolithic  $\text{MoSi}_2$  is handleable at room temperature, both as fine grained and single crystal material[7]. On the other extreme highly anisotropic hexagonal  $\text{Ti}_5\text{Si}_3$  is best produced as ultra-fine grained material with macroscopic isotropy [8].

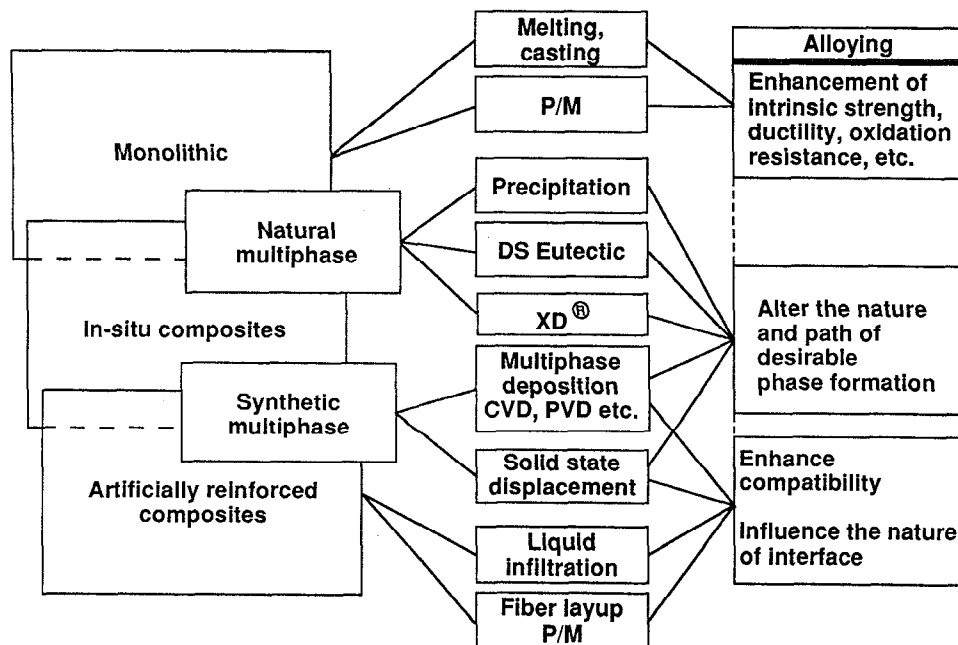


Figure 1 - Schematic overview of strategies for the development of intermetallic structural materials.

Alternatively, the silicides may be largely considered as a dominant part of a two phase composite microstructure produced in-situ, or artificially. Here the major driver for compositing is lack of room temperature toughness rather than strength. When the two phase composite microstructure is produced using natural phase separation mechanisms such as solid state precipitation or directional solidification of an eutectic, the resulting composite is referred to as in-situ. In a sense superalloys and nickel base eutectic alloys are ideal examples of in-situ composites. To the list of in-situ processes, the proprietary XDR<sup>®</sup> process [9] and synthesis of MoSi<sub>2</sub>/SiC composites using Mo<sub>2</sub>C and Si powders may be added, as novel processing approaches.

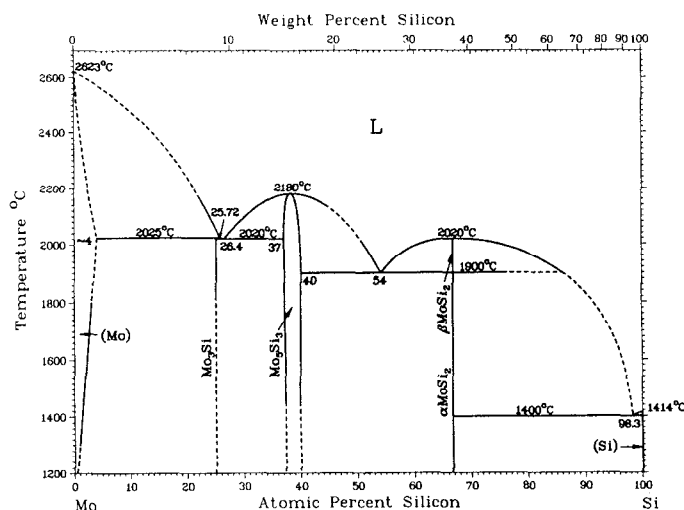
The latitude for varying the distribution and the volume fraction of the second phase may be broadened if the two phase microstructure is produced synthetically, typically as microlaminates, using techniques such as controlled chemical vapor deposition (CVD). At this stage, however, such techniques are unable to produce bulk materials.

In artificial composites, the individually identifiable, matrix and reinforcement materials with optimized, intrinsic properties, are judiciously juxtaposed. MoSi<sub>2</sub> reinforced with single crystal alumina monofilaments (Saphikon) may be cited as a model example. In concept, this is attractive on the assumption that the balance of all other properties including toughness may be achieved once one of the most oxidation resistant refractory intermetallics is reinforced with the strongest available fiber. In terms of improving toughness, however, greater success has been achieved with ductile reinforcements. This has been the focal point of many of the recent activities.

Further, as emphasized in Figure 1, alloying can be a useful strategy. In monolithic materials, the intrinsic properties such as strength, ductility, and oxidation resistance, may be enhanced much the same manner it has been attempted for nickel base intermetallics Ni<sub>3</sub>Al and NiAl. In parallel, however, MoSi<sub>2</sub> offers limited flexibility, partially being a line compound as seen in the binary phase diagram reproduced in Figure 2.

In in-situ composites, alloying may alter the nature and path of desirable phase formation. With reference to the Mo-Si binary phase diagram in Figure 2, any of the two phase regions Mo/Mo<sub>3</sub>Si, Mo<sub>3</sub>Si/Mo<sub>5</sub>Si<sub>3</sub>, and Mo<sub>5</sub>Si<sub>3</sub>/MoSi<sub>2</sub> may be considered potential in-situ composites. In artificially reinforced composites, alloying may be used to enhance the reinforcement/matrix compatibility or to influence the nature of the interface. Clearly the far reaching influence of alloying cannot be underestimated but this aspect has not been fully explored for silicides[11].

Figure 2 - Mo-Si binary phase diagram.



### Formation of Silicides

The principal aspects of the formation of useful silicides can be gleaned from the Mo-Si binary phase diagram presented in Figure 2. There are primarily three groups of refractory metal silicides: (1) Silicon rich, and consequently most oxidation resistance disilicides such as MoSi<sub>2</sub>, (2) complex, some of the highest melting intermetallics, 5-3 silicides such as Mo<sub>5</sub>Si<sub>3</sub> and (3) refractory metal rich cubic A15 intermetallics such as Mo<sub>3</sub>Si.

To grasp the alloying behavior of these silicides in some cohesive manner, it is best to consider the projection of a pseudo-quaternary phase diagram with Si at the apex, onto the base ternary formed by three groups of transition elements, as shown in Figure 3. Each group of elements loosely consists of transition elements forming iso-structural silicides. Figure 3 is not intended to represent all silicides or Si containing phases. Many topologically closed packed (TCP) phases (Laves and Sigma), known to be undesirable phases in superalloys are ignored, and so are the many intermediate silicides in many other binary systems such as Mn-Si.

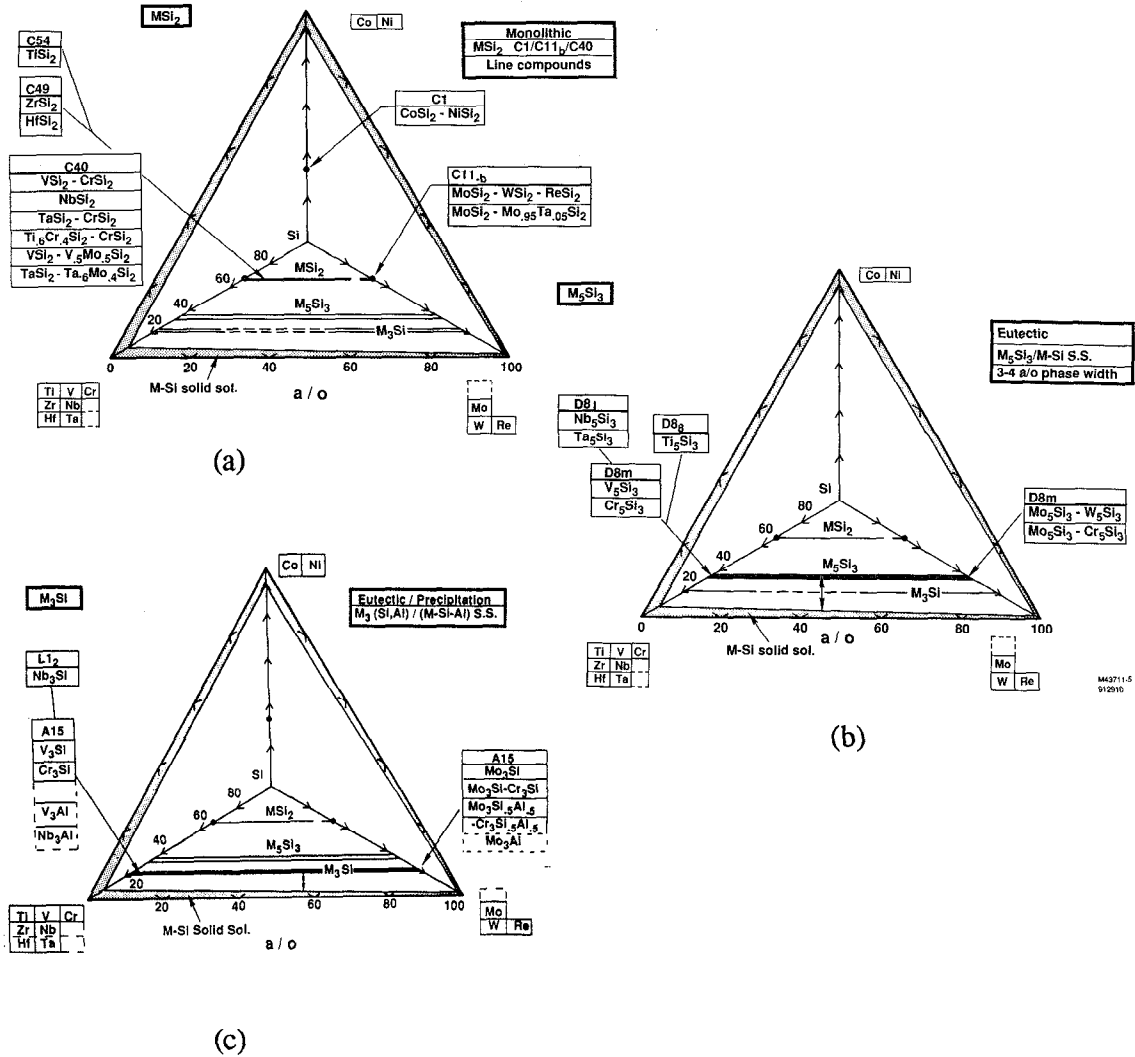


Figure 3 - Projection of a pseudo-quaternary phase diagram summarizing the formation of useful silicides: (a) disilicides, (b) 5-3 silicides, and (c) monosilicides.

As summarized in Figure 3(a), there are primarily three groups of disilicides: Ni and Co disilicides with the cubic  $\text{CaF}_2$  (C1) structure, Mo, Re and W disilicides with the tetragonal  $\text{C11}_b$  structure, and Cr and Ti groups of disilicides with the hexagonal C40 and C54 structures. Among these, the disilicides with the C1 and the  $\text{C11}_b$  structures, show limited solubility of other elements. In addition, the Ni and Co based cubic silicides with the C1 structure are low melting, and bear no simple crystal structure relationship to other disilicides.

In contrast, the disilicides with  $\text{C11}_b$ , C40 and C54 structures are closely related by differing stacking sequence of the closed packed planes as shown in Figure 4. The nature of stacking sequence is reminiscent of the aluminides with the  $\text{L1}_2$  ( $\text{Ni}_3\text{Al}$ ) and related non-cubic  $\text{DO}_{19}$ ,  $\text{DO}_{24}$ ,  $\text{DO}_{22}$  and  $\text{DO}_{23}$  structures. Beyond the generic analogy, however, there is a clear geometrical difference in the stacking of silicides versus aluminides as compared in Figure 5, with probably a significant implication for deformation behavior. While in the case of aluminides the atoms fit into the natural pockets between three contiguous atoms (Figure 5(b)),

the atoms in the next layer in the disilicides occupy the saddle positions between two Si atoms (Figure 5(a)). Consequently, for the simpler stacking sequences in silicides with the C11<sub>2</sub> or C40 structures, Si atoms remain closely bonded in sheets normal to the stacking plane, precluding the kind of closed packed slip we are used to consider with reference to the ordered g' with L1<sub>2</sub> structure. Only for the C54 (TiSi<sub>2</sub>) structure, with all four equivalent stacking positions used, that Si-Si chain is interrupted with refractory metal atoms as shown in Figure 6(a). However, deformation behavior of silicides with such structures has not been fully explored. In spite of the complexity, the disilicides with the C40 structure, by far presents the broadest latitude in alloying. Note the disilicides present no known opportunities for in-situ ductile phase toughened composites with a terminal metal base solid solution. They may form brittle-brittle in-situ composites with neighboring 5-3 silicides, however.

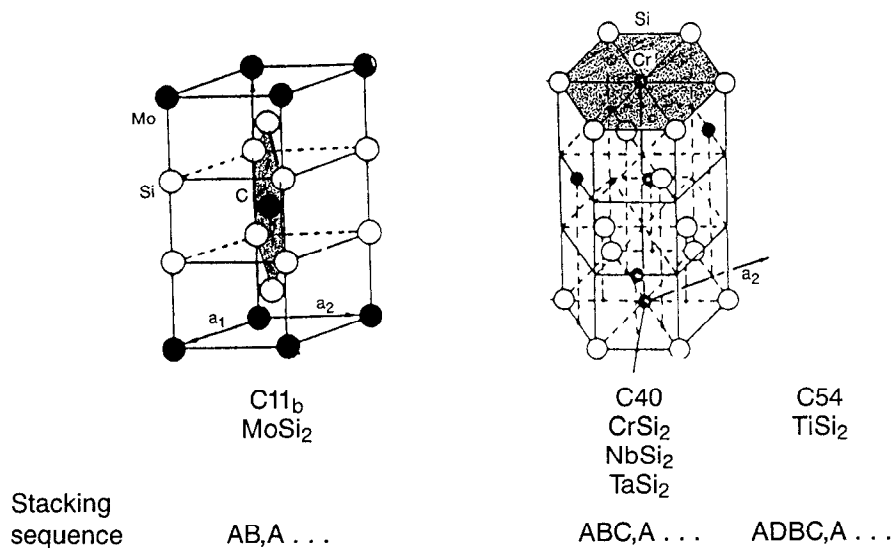


Figure 4 - Interrelationship between C11<sub>b</sub>, C40 and C54 structures in terms of the stacking sequence of the closed packed planes.

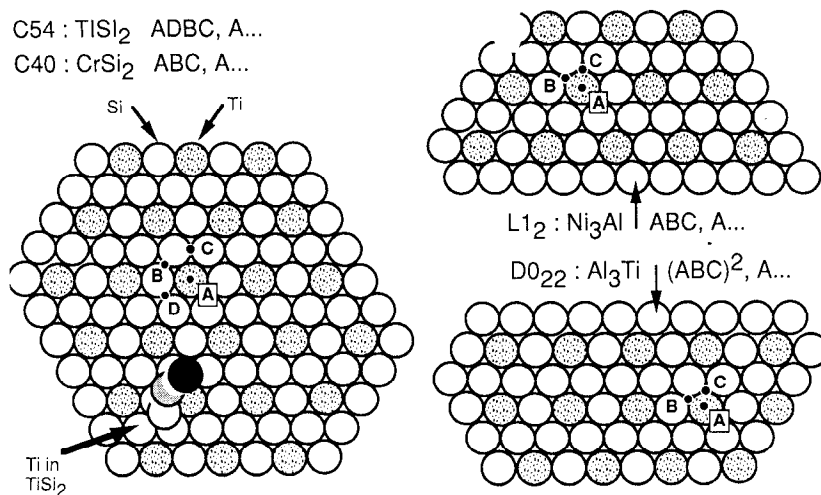


Figure - 5 Comparison of stacking in (a) disilicides vs. (b) trialuminides.

With the 5-3 silicides, as shown in Figure 3(b), the alloying opportunities are broadened and this may be even further extended if the interrelationships between various complex D8<sub>x</sub> structures were known. In many systems, with the suppression of other silicides or TCP phases, a eutectic is formed between the 5-3 silicide and the refractory metal solid solution.



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