

## 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].

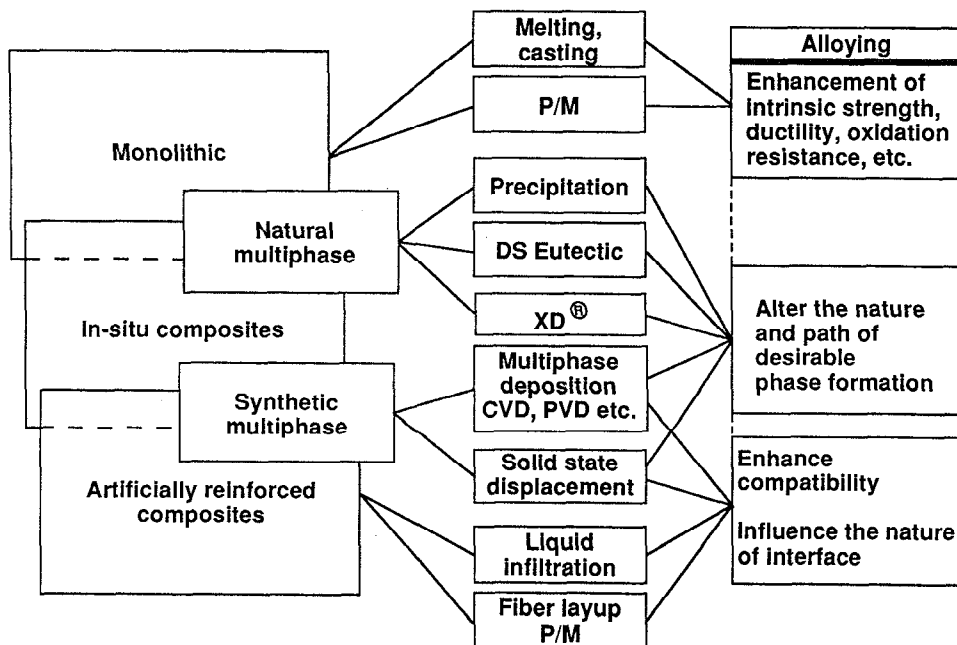


Figure 1 - Schematic overview of strategies for the development of intermetallic structural materials.

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.

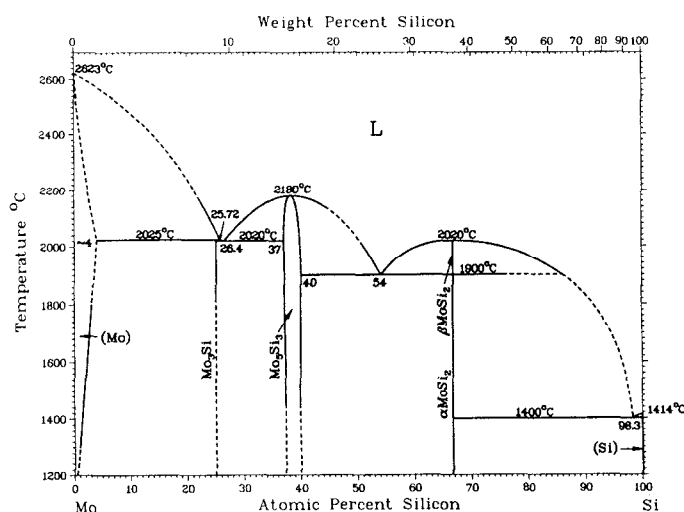
The latitude for varying the distribution and the volume fraction of the second phase may be broadened if the two phase microstructure is produced synthetically, typically as microlaminates, using techniques such as controlled chemical vapor deposition (CVD). At this stage, however, such techniques are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

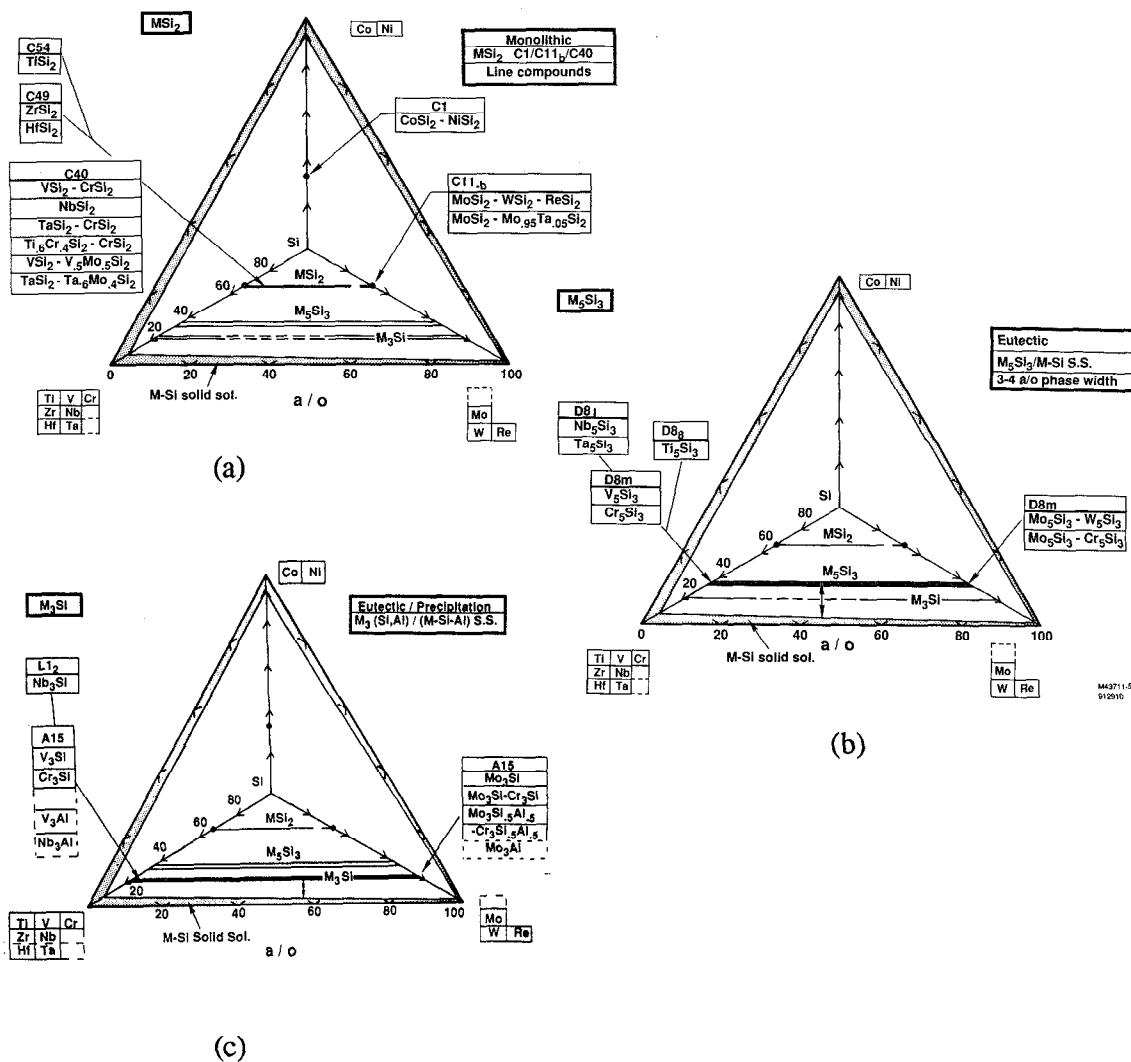


Figure 3 - Projection of a pseudo-quaternary phase diagram summarizing the formation of useful silicides: (a) disilicides, (b) 5-3 silicides, and (c) monosilicides.

As summarized in Figure 3(a), there are primarily three groups of disilicides: Ni and Co disilicides with the cubic CaF<sub>2</sub> (C1) structure, Mo, Re and W disilicides with the tetragonal C11<sub>b</sub> structure, and Cr and Ti groups of disilicides with the hexagonal C40 and C54 structures. Among these, the disilicides with the C1 and the C11<sub>b</sub> 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 C11<sub>b</sub>, 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 L1<sub>2</sub> (Ni<sub>3</sub>Al) and related non-cubic DO<sub>19</sub>, DO<sub>24</sub>, DO<sub>22</sub> and DO<sub>23</sub> 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.

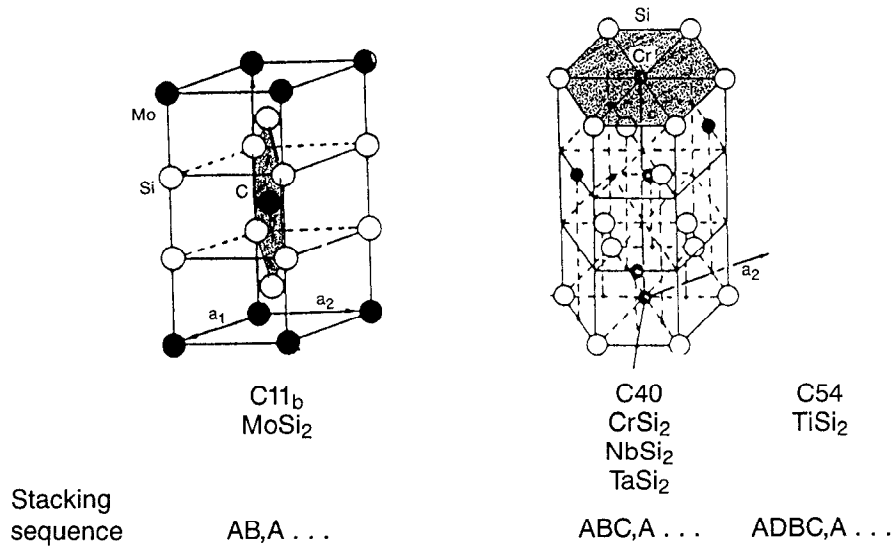


Figure 4 - Interrelationship between C11<sub>b</sub>, C40 and C54 structures in terms of the stacking sequence of the closed packed planes.

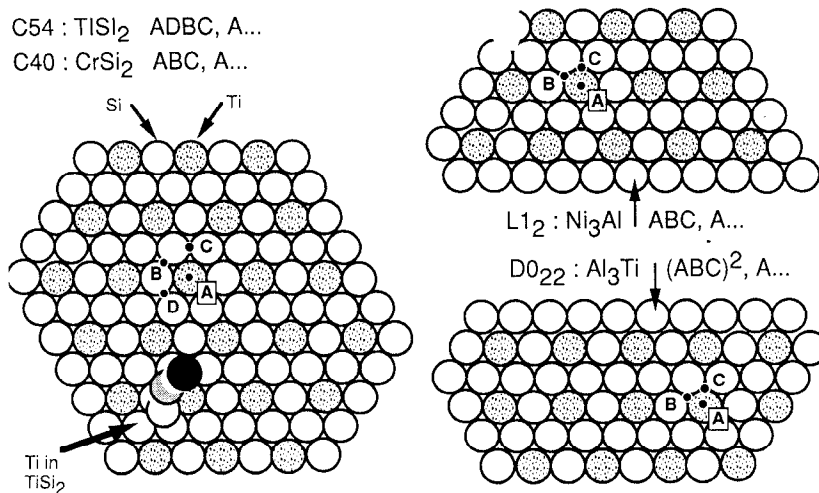


Figure - 5 Comparison of stacking in (a) disilicides vs. (b) trialuminides.

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.

Nb/Nb<sub>5</sub>Si<sub>3</sub> and Ti/Ti<sub>5</sub>Si<sub>3</sub> are two such systems currently being explored [12,13]. The complexity of the structure of 5-3 silicides can be surmised from the structure of D8<sub>8</sub>(Ti<sub>5</sub>Si<sub>3</sub>, prototype Mn<sub>5</sub>Si<sub>3</sub>), schematically shown in Figure 6(a). In the D8<sub>8</sub> structure part of the refractory element atoms (Ti (I) in Figure 6) form chains along the hexagonal axis, with the second group of atoms of refractory elements (Ti(II) in Figure 6) forming columns of octahedrons connected along the c-axis, with the octahedral interstices partially or completely filled by interstitials.

Lastly the monosilicides with the A15(Cr<sub>3</sub>Si) structure form the third largest group of silicides occurring next to the refractory metal solid solution as shown in Figure 3(c). For this group of cubic silicides, alloying with other refractory metals is limited, though complete solid solubility exists between Cr<sub>3</sub>Si and Mo<sub>3</sub>Si. The alloying possibilities are expanded, however, when considered in conjunction with isostructural aluminides such as Nb<sub>3</sub>Al [14]. The crystal structure of the A15(Cr<sub>3</sub>Si) is presented in Figure 6(b). Note that in the case of the A15 structure, the atoms of the refractory element form three orthogonal chains, which crisscross the body centered cubic arrangement of non-transition elements. The A15 structure is considered the simplest of the topologically closed packed(TCP) structures, which by definition should have no octahedral interstitialcies. This aspect is novel to those used to closed packed fcc structure of nickel base alloys with little solubility for interstitial elements. However, in the context of the open bcc structure of refractory metals as high temperature structural materials, the solubility of interstitial elements and their effect on the strength, stability and environmental resistance assume critical importance.

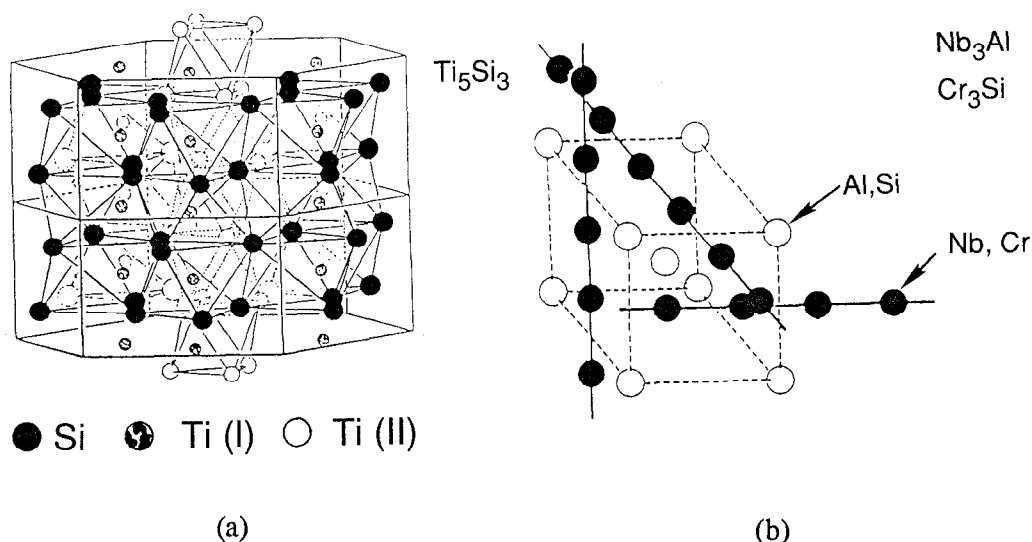


Figure 6 - Crystal structure of (a) Ti<sub>5</sub>Si<sub>3</sub> (D8<sub>8</sub>, Prototype Mn<sub>5</sub>Si<sub>3</sub>) and (b) Cr<sub>3</sub>Si(A15).

#### Alloying of Silicides and Other Silicides

Among the non-transition elements such as Al, Ga, Ge, Sn, As and Sb, with which silicides may be alloyed, Al is apparently most attractive from the stand point of enhancing the environmental resistance and imparting more metallic character to the silicides, but the benefits of alloying with Al are not clearly defined. At any rate, with the historical experience base available with aluminides in superalloys, understanding a link between the aluminides and silicides poses an interesting problem. There are also other silicides with interesting structures, especially the defect disilicides based on MnSi<sub>2-x</sub>, with long chain polytypes similar to SiC. . For more details on these aspects, the reader is referred to a recent appraisal of other silicides[11].

#### Comparison of Physical and Mechanical Properties

Owing to their semi-metallic bonding characteristics, silicides present an interesting combination of physical and mechanical properties. For example silicides such as CrSi<sub>2</sub> and

ReSi<sub>2</sub> are known to be semi-conductors at high temperatures[11]. This presents an additional opportunity for the development of 'smart' structural materials for high temperature applications. The following discussion, however, is limited to the properties of immediate interest as high temperature structural materials and is intended to provide the readers with a comparative feel for physical properties of silicides vis a vis superalloys.

### Melting Point and Density

For several typical silicides and silicide based systems, physical and mechanical properties are compared in Table I. To provide a reference, properties of typical nickel base alloys, ceramics and metals are also included. Note that certain disilicides present a density advantage over superalloys. Most other silicides are attractive for their high melting points only with potential for high strength and enhanced creep resistance.

Table I. - Comparison of physical and mechanical properties of silicides.

Silicide System(s)	Crystal Structure	Melting Point, C	Density gm/cm <sup>3</sup>	Coefficient of thermal expansion (10 <sup>6</sup> /°C) (20-1000 °C)			Room Temp. Fracture Toughness MPa. m <sup>1/2</sup>
				α1	α2	α3	
Ni	Cubic fcc	1453	8.9		16.3		
PWA 1480	fcc/L12	1296	8.69		15.8		>50
CoSi <sub>2</sub>	Cubic C1	1326	4.98				
V <sub>3</sub> Si	Cubic A15	1973	5.71		12.5		
Cr <sub>3</sub> Si	Cubic A15	1773	6.46		10.5		
Al <sub>2</sub> O <sub>3</sub>	Cubic	2050	4.0		9.1		
MoSi <sub>2</sub>	Tetragonal C11b	2030	6.24	8.25		9.05	5-8
ReSi <sub>2</sub>	Tetragonal C11b			6.6		6.6?	
Ti	C.P.Hexagonal			9.6		10.7	
Ti <sub>5</sub> Si <sub>3</sub>	Hexa. D8m	2130	4.32	3.05		10.7	
Ti/Ti <sub>5</sub> Si <sub>3</sub>	(Eutectic)	1332					11
Nb <sub>5</sub> Si <sub>3</sub>	Hexa. D8b	2484	7.16				
Nb/Nb <sub>5</sub> Si <sub>3</sub>	(Eutectic)	1883					10-22
CrSi <sub>2</sub>	Hexa. C40	1477	4.63				
Ta <sub>5</sub> Si <sub>3</sub>	Hexa.			5.5		8	
Ta <sub>5</sub> Si <sub>3</sub> (Nowotny)	Hexa.			6.3		6.6	
TaSi <sub>2</sub>	Hexa. C40	2204	9.08	8.9		8.8	
TiSi <sub>2</sub>	Orth. C54	1542	4.04	?	?	?	

### Thermal Expansion and Elastic Modulus

Those familiar with the history of directionally solidified and single crystal superalloys are well aware of the concurrent improvement in thermal mechanical fatigue life(TMF), with almost 30 % reduction in elastic modulus along the <100> oriented turbine blade axis, compared to polycrystalline superalloys. TMF occurs in complex components subjected to thermal transients or hot spots. The magnitude of the resulting thermal macrostress is proportional to the product of the elastic modulus, coefficient of thermal expansion (CTE), and temperature gradient. Owing to the macrostress damage accumulates, either if the material is poor in creep at high temperature or brittle at room temperature.

In addition to the problems encountered with superalloys and brittle coatings on them, the non-cubic nature of some of the silicides adds another complication. CTE is isotropic for cubic materials but it is expected to be anisotropic in non-cubic material. In materials with an anisotropic CTE, the residual microstress occurs in the grain boundaries below the ductile to brittle transition temperature (DBTT), owing to differences in thermal expansion along the same direction in neighboring grains. Such a stress at room temperature is a function of the elastic modulus, anisotropy in CTE, grain size and the DBTT. Such microstresses not only

affect the durability of the material but the processibility as well. In principle there is no way to eliminate the residual microstress in brittle polycrystalline materials with a highly anisotropic CTE. In all situations low modulus and low and isotropic values of CTE are beneficial.

To appreciate the magnitude of anisotropy, the CTE for several silicides are listed in Table 1. Note that no data has been found for any orthorhombic disilicide, for which three CTE's must be specified. The data suggest, near isotropy of the CTE for the non-cubic disilicides, but high anisotropy for the hexagonal 5-3 silicides. This is consistent with the experimental observations of transgranular cracking in  $Ti_5Si_3$ , as shown in Figure 7(a), with no reported evidence of such cracking in any disilicides including  $MoSi_2$ . None the less the non-cubic nature of  $MoSi_2$  is obvious from the revelation of grain structure under polarized light as shown in Figure 7(b).

While the CTE is expected to be anisotropic for non-cubic silicides, the magnitude of the anisotropy is not predictable a priori. No approximate correlations have been developed between the extent of anisotropy and the nature of atomic ordering for specific crystal structure type. The restoration of isotropy for the CTE of Nowotny  $Ta_5Si_3$  as quoted in Table 1 suggests there is hope to improve the situation with alloying.

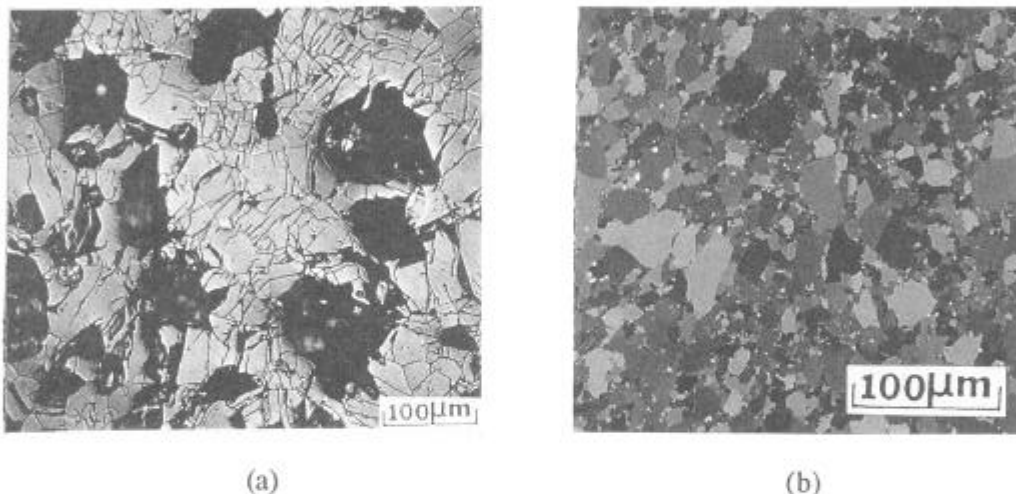


Figure 7 - Non-cubic structure of silicides leading to  
(a) transgranular microcracking in as-cast  $Ti_5Si_3$ .  
and (b) grain structure in  $MoSi_2$  revealed under polarized light.

The average elastic modulus for several silicides are plotted as a function of temperature in Figure 8. For purposes of comparison the extent of elastic anisotropy at room temperature for nickel base alloys, Nb and Al is also shown. The data have been collected from various sources and in most cases, having been measured by acoustic methods, are considered very reliable. Some of the results are based on four point bend tests and are indicated as such[2]. With the notable exception of compounds with the  $C11_b$  structure ( $MoSi_2$ ,  $WSi_2$ ), all silicides have moduli comparable to at least polycrystalline nickel base alloys. Thus on the account of elastic modulus the scenario is not favorable for silicides in comparison to superalloys, but far more attractive compared to ceramics.

### Thermal Conductivity

Though of secondary importance, a material with high thermal conductivity can dissipate thermal transients more rapidly thereby improving its performance at high temperature under thermal gradients. This has been one of the motivations behind the development of single crystal NiAl as a high temperature structural material [6], in spite of only a moderate advantage in melting temperature over nickel base superalloys. The thermal conductivity data for NiAl and nickel-base superalloys, from reference [6], are compared with data for  $TiSi_2$  and  $MoSi_2$ , from other sources[11], in Figure 9. Note that if extrapolated to temperatures above  $1000^\circ C$ , the thermal conductivities of both silicides are comparable to nickel- base superalloys. It must

be emphasized that material selection on the thermal conductivity is somewhat sensitive to the design of cooling scheme in critical component like turbine blade. In an overall sense, however, silicides do not appear unattractive on this account.

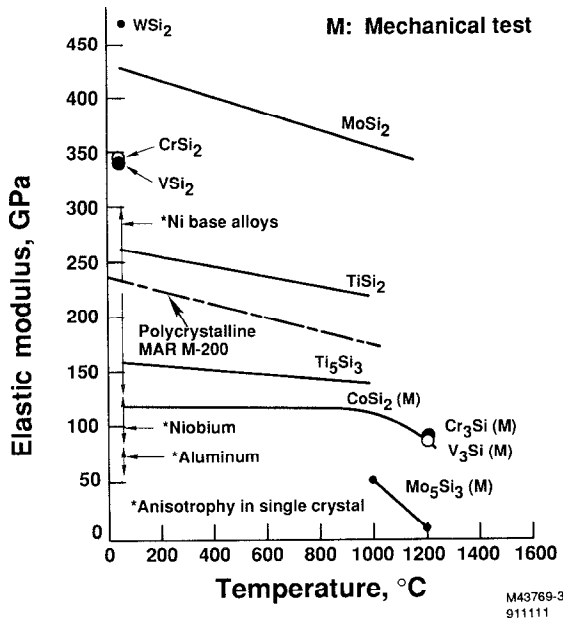


Figure - 8 Comparison of average elastic modulus as a function of temperature

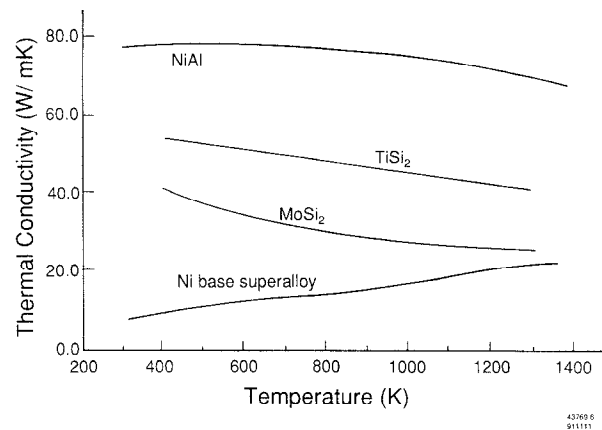


Figure - 9 Comparison of thermal conductivities as a function of temperature.

### Strength, Ductility and Toughness

At the exploration stage the strength of silicides may be evaluated directly using bend tests or in compression, or indirectly compared using hardness measurements. For brittle materials, however, these kinds of measurements are only worth the comparative guidance they provide. It is not uncommon to find a large discrepancy between the strength measured in bending versus that in compression, especially at low temperature. Even at high temperature, where silicides show some plasticity, the strength can be very sensitive to microstructure and processing history. Fortunately, in many silicides the deformation behavior of single crystals has been studied and operative slip systems have been identified[15]. Such data on single crystal afford the best comparison with nickel base superalloys as plotted in Figure 10. Note that as in superalloy single crystals, the strength anisotropy also exists in single crystal  $\text{MoSi}_2$ . At  $1300^\circ\text{C}$  ( $2372^\circ\text{F}$ ), the strength of 500 MPa (72 ksi) for the strongest  $\langle 001 \rangle$  oriented  $\text{MoSi}_2$  single crystal is comparable to the strength of superalloys at  $1000^\circ\text{C}$  ( $1832^\circ\text{F}$ ). The bending over of the strength curves for  $\text{MoSi}_2$  and the absence of data below  $1000^\circ\text{C}$  are indicative of the ductile to brittle transition temperature (DBTT). For comparison, the DBTT of polycrystalline NiAl is around  $500^\circ\text{C}$ .

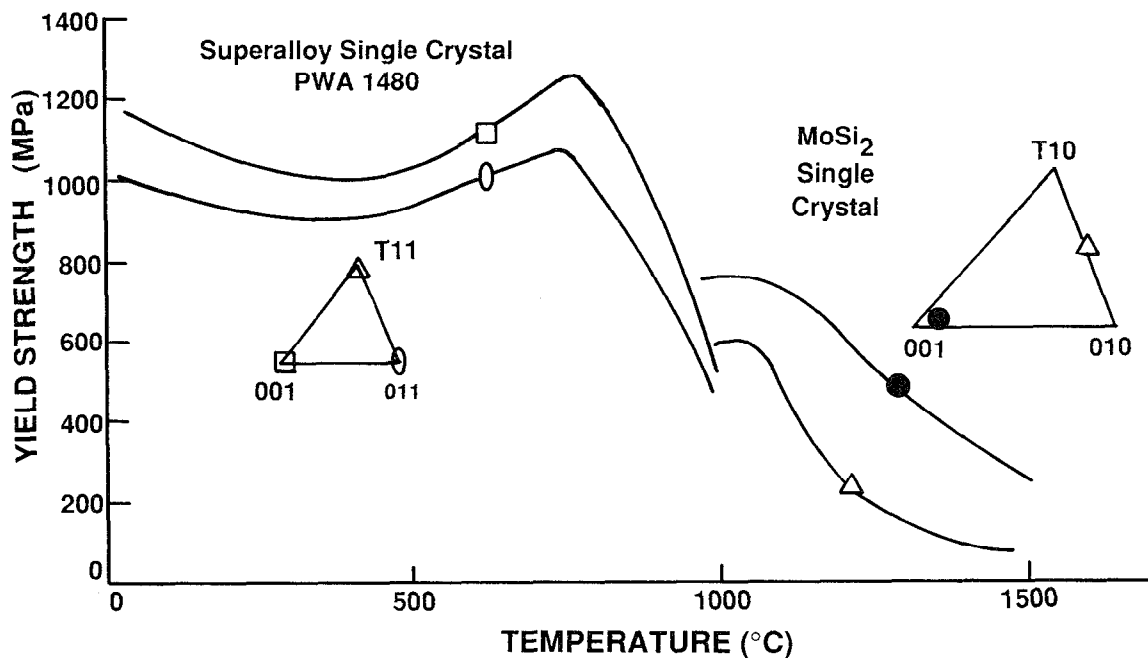


Figure - 10 Comparison of yield strength versus temperature between superalloys and MoSi<sub>2</sub> single crystals.

There is no well defined approach proposed for lowering the DBTT of monolithic silicides, and this is not surprising, given the infant state of development. However, the prospect of improving the room temperature toughness, by using the ductile phase toughening approach appears promising. Use of an in-situ approach, is best demonstrated for the unidirectionally solidified Ti/Ti<sub>5</sub>Si<sub>3</sub> eutectic and the hot worked Nb/Nb<sub>5</sub>Si<sub>3</sub> hyper-eutectic compositions as listed in Table I. In the former case the fracture toughness has been shown to improve from 2 MPa.m<sup>1/2</sup> for the monolithic material to 12 MPa.m<sup>1/2</sup> for the two phase material at room temperature. At 400°C, the two phase material has an even higher fracture toughness of 25 MPa.m<sup>1/2</sup>. Similar gain in fracture energy has been shown for MoSi<sub>2</sub> reinforced with alumina coated NS-Mo alloy fibers[16].

#### High Temperature Creep Resistance

For several binary and alloyed silicides, the minimum creep rate in compression versus stress is reproduced from Reference [11] in Figure 11. A range of minimum creep rates for the current generation of nickel-base superalloy single crystals is shown at 1000°C[17], for the purpose of comparison. Based on a direct comparison at 1000 C, the creep resistance of Ti<sub>5</sub>Si<sub>3</sub> and Mo<sub>5</sub>Si<sub>3</sub> is comparable to superalloys. A reasonable extrapolation of the creep rates at 1200 C to 1000°C, show V<sub>3</sub>Si is considerably weaker. However, MoSi<sub>2</sub> and Cr<sub>3</sub>Si, appear to be promising with extrapolated creep rates comparable to superalloys. This is further confirmed with alloying. Equivalent minimum creep rate is attained at 200 C higher temperature upon alloying of MoSi<sub>2</sub> with Re. In the Mo modified Cr<sub>3</sub>Si (Cr-39 a/o Mo-23 a/o Si) alloy, as plotted in Figure 11, the minimum creep rate at 1200 C is comparable to superalloys at 1000 C at 172 MPa. Addition of SiC whiskers also appears to be beneficial. Caution must be exercised in interpreting the compressive creep data presented here any further. It has been shown that like ceramic materials, in tension an order of magnitude increase in creep rate results due to grain boundary cavitation in MoSi<sub>2</sub> [7].

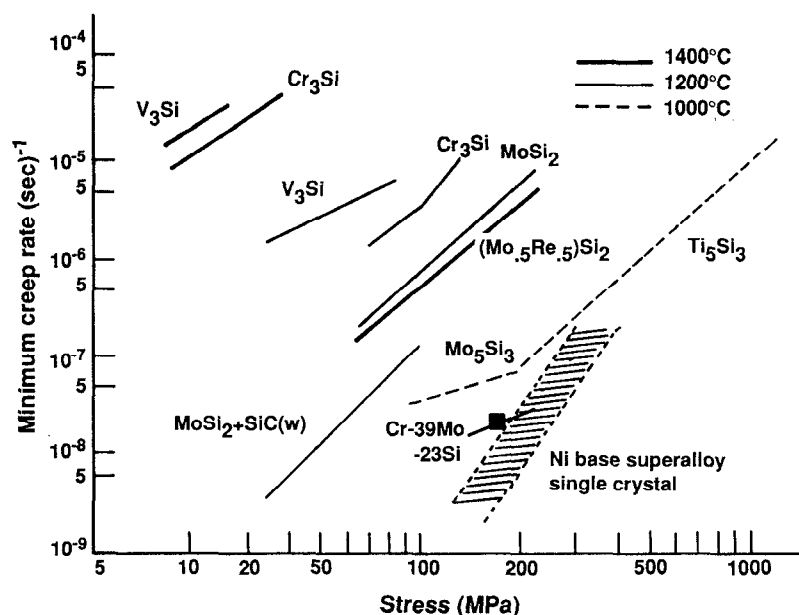


Figure - 11 Comparison of minimum creep rate in compression vs. stress for several silicides and their alloys.

### Environmental Resistance

In contrast to superalloys, it is not so much the high temperature oxidation resistance of silicides but the low temperature 'pest' disintegration or accelerated oxidation are critical problems.

**High Temperature Oxidation Resistance:** Based on earlier work and recent studies [11,14,17], it may be concluded that almost all disilicides possess excellent oxidation resistance. However, while MoSi<sub>2</sub> is known to form pure tetragonal SiO<sub>2</sub>, most other disilicides form mixed oxides; although the formation of mixed oxides in some cases is not necessarily detrimental as has been seen for CoSi<sub>2</sub>[11,14]. It is now well recognized that the volatility of MoO<sub>3</sub> plays an important role in the oxidation behavior of MoSi<sub>2</sub>[18]. Thus while oxidation of other disilicide such as TaSi<sub>2</sub> is observed to be qualitatively similar to MoSi<sub>2</sub>, the high thermodynamic stability and low volatility of Ta<sub>2</sub>O<sub>5</sub> result in much higher temperature being required for SiO<sub>2</sub> to be formed[18].

Among 5-3 silicides, only Ti<sub>5</sub>Si<sub>3</sub> is known to have reasonable oxidation resistance[11]. Mo<sub>5</sub>Si<sub>3</sub> and Nb<sub>5</sub>Si<sub>3</sub> are known to disintegrate rapidly at high temperature[19,14]. Consistent with these observations, alloying of Nb<sub>5</sub>Si<sub>3</sub> with Ti shows significant improvement in oxidation resistance[19]. Alloying with Ta, Mo, Zr and Hf is not beneficial and alloying with Al is only marginally better in conjunction with Ti. Among a limited number of monosilicides, only Cr<sub>3</sub>Si is known to possess excellent oxidation resistance, though somewhat poorer than MoSi<sub>2</sub>[14].

**The Pest Effect:** A total disintegration of some of the silicides at low temperatures (500°C-900°C), is known as the 'pest' effect. The exact nature of underlying mechanisms for the 'pest' phenomena are just being addressed[18]. It is now well established that cast MoSi<sub>2</sub> with uncontrolled grain structure and pre-existing cracks 'pest' profusely. In contrast, in the absence of external stress, single crystals and hot pressed or hot isostatically pressed(HIP) fine grained MoSi<sub>2</sub> do not disintegrate, though show some signs of accelerated oxidation resistance at low temperatures[18]. Clearly the 'pest' effect in MoSi<sub>2</sub> is microstructure sensitive and consequently dependent on the fabrication methods. In a broader picture, there is no resounding evidence to suggest that 'pest' is a major problem with cubic aluminides or silicides

such as  $\text{Cr}_3\text{Si}$  and  $\text{CoSi}_2$ .

There is no question that environmental factors, alloy chemistry and oxidation kinetics, all play important roles in controlling the pest effect but residual internal stress is also a necessary condition. As previously discussed, residual microstress at grain boundaries can build up in non-cubic brittle materials with highly anisotropic CTE's. If the material is single crystal or highly textured, the effect of an anisotropic CTE can be mitigated geometrically. Qualitatively the pest effect may be correlated with three factors - DBTT, anisotropy of CTE, and the nature of grain boundary structure[11]. Many unrecognized virtues of the cubic structure of superalloys cannot be better appreciated.

### Processing of Silicides

As discussed with reference to Figure 1, there are at least two clear options open to develop silicide based composites, and both are being pursued. For the artificial composite approach,  $\text{MoSi}_2$  is an ideal oxidation resistant matrix and the goal is to process the composite to form stable composite microstructures with improved fracture toughness. In pursuing this approach one must consider the fiber/matrix compatibility. The incompatibility may result either from thermochemical instability or thermomechanical mismatch due to large differences in CTE or elastic modulus. As shown in the micrograph of  $\text{MoSi}_2/\text{SCS-6}(\text{SiC})$  fiber reinforced composite in Figure 12(a), radial cracking occurs upon processing due to large mismatch in CTE. As shown in Figure 12(b), using strong single crystal Saphikon ( $\text{Al}_2\text{O}_3$ ) monofilaments, a good composite can be consolidated using pre-alloyed powder, but the strong fiber matrix bonding does not lead to fiber pull-out and show no improvement in fracture toughness[16]. Compared to the SCS-6 and Saphikon monofilaments, the scale of the microstructure can be reduced, as shown in Figure 12(c), using FP alumina fiber tow, but the fiber damage must be avoided by lowering the processing temperatures with the use of stoichiometric mixture of elemental powders[22]. It is well accepted that alumina is compatible with  $\text{MoSi}_2$  with insignificant CTE mismatch and minimal interface reaction, but unavailability of stronger fiber tow or finer and economically viable single crystal monofilaments hinder further use of strong reinforcement.

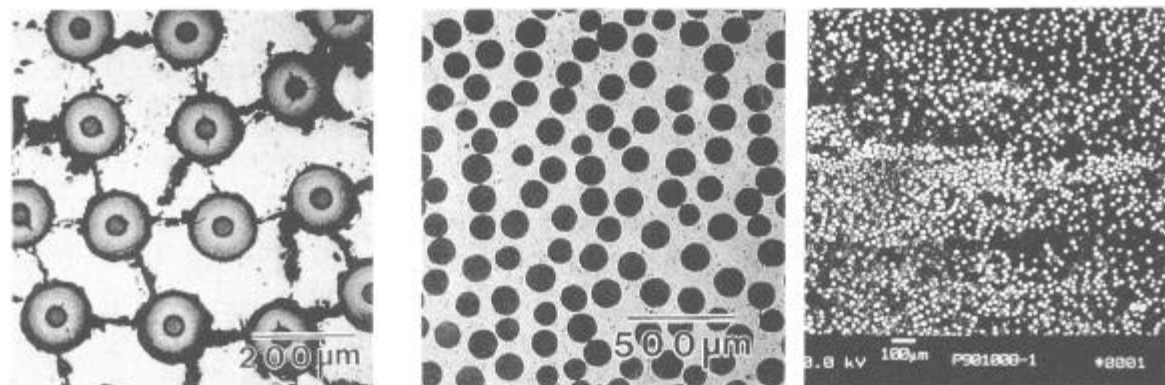


Figure 12 - Microstructure of  $\text{MoSi}_2$  based composites reinforced with (a) SCS-6( $\text{SiC}$ ) monofilaments, (b) Saphikon (alumina single crystal) monofilaments, and (c) FP alumina fiber tow.

Alternatively, the use of ductile refractory metal based filaments is considered a preferred approach for improving toughness of  $\text{MoSi}_2$ . In this approach, however, the high temperature fiber/matrix interdiffusion, fiber oxidation and CTE mismatch become serious issues. Feasibility of addressing these issues have been demonstrated with sol-gel alumina coated W-3%Re filaments in a  $\text{MoSi}_2+\text{SiC}$  hybrid matrix[16].

Besides fibers, a host of other phases are being considered as particulate addition to  $\text{MoSi}_2$ [1], but while naturally the high temperature ultimate strength and creep resistance can be improved by such dispersion hardening approaches, the primary issue of lack of toughness is not addressed. If earlier failure of cermets, and a measured success of oxide dispersion

strengthened (ODS) superalloys are any reminder; dispersion strengthening, though conceptually simple is not reliable for dynamically critical components. Poor microstructural control besets the progress of such seemingly simple composite approaches including fiber reinforced composites where additionally the high cost of production is likely to demand a larger payoff for critical applications.

As opposed to artificial composites the in-situ composite approach becomes system specific but naturally provides excellent microstructural control. As has been discussed with reference to Figures 2 and 3,  $\text{MoSi}_2$  does not offer any opportunity to form a ductile second phase. The two phase field between other refractory rich silicides and refractory metal solid solution must be considered as has been reported with  $\text{Nb/Nb}_5\text{Si}_3$  [12] and  $\text{Ti/Ti}_5\text{Si}_3$  [13]. In these cases, the processing include a combination of heat treatments, hot working or directional solidification. Though conventional in nature, these processes as applied to high melting silicides present other problems. For example with a lack of suitable ceramic container, the directional solidification must be carried out in a containerless manner, either using induction, electron or optical float zone [20,21]. Microstructures of  $\text{Cr/Cr}_3\text{Si}$  eutectic presented in Figure 13 bring forth the fine scale and uniformity produced by cold crucible directional solidification [20].

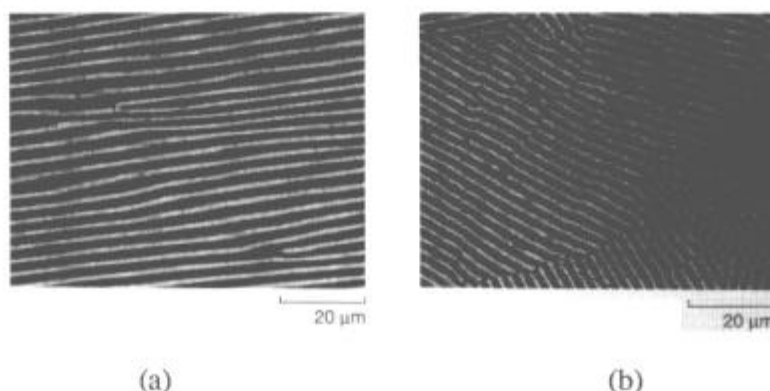


Figure 13 - Positive-polarity BSE image of  $\text{Cr-Cr}_3\text{Si}$  eutectic composite .  
(a) Longitudinal section. (b) transverse section.

### Summary

Refractory metal silicides with almost metal-like physical properties and significantly higher melting points have potential for developing high temperature structural materials beyond superalloys, provided their inherent lack of ductility or toughness is restored through composite approaches. While  $\text{MoSi}_2$  with its excellent oxidation resistance is an ideal matrix material for conventional fiber reinforced composites, other silicides too offer ample opportunities to produce ductile phase toughened in-situ composites with highly controlled microstructures. Where the conventional composite approach is hindered by the availability of suitable high temperature fibers and fiber coatings, the in-situ composites relying on directional solidification need containerless processing.

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