Development of in-situ toughened silicon-rich alloys:  
a new class of castable engineering ceramics

by

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ABSTRACT

Despite having a broad set of desirable properties, silicon’s potential as a primary constituent in a structural material has not yet been realized because of its extremely low fracture toughness. Motivated by the microstructural design techniques used in toughening inherently brittle ceramic materials, this work aims to develop a silicon-rich alloy with microstructural features that provide for the same types of toughening mechanisms displayed by technical ceramics. In order to add true commercial value to these silicon-based alloys, however, the alloys must be processed using methods more flexible and less expensive than the powder processing routes currently used for engineering ceramics. This thesis will discuss the development of a class of castable silicon-based alloys referred to as silicon-disilicide (Si-XSi2) composites, which naturally form a microstructure composed of a silicon matrix and reinforcing disilicide (XSi2) phase during solidification (where X is a transition metal). Experimental work is performed to characterize the thermal, microstructural, and fracture properties of a specific set of Si-(Cr,V)Si2 alloys which are based on the Si-CrSi2-VSi2 system. First, a reliable thermodynamic description of the Si-CrSi2-VSi2 system is obtained, from which the relevant phase diagram is determined. Comparison between simulated solidification paths and experimentally observed microstructures demonstrates the use of the thermodynamic database to predict the phase evolution of the alloys during processing. Long-crack fracture toughness measurements made through chevron-notched beam (CNB) tests show that the toughness of the composite alloys are over 2-3 times that of unalloyed silicon, with in-situ tests revealing the role of microstructural toughening (via crack deflection and crack bridging) on the enhanced fracture properties. Ball-on-disk experiments reveal an order of magnitude improvement in the wear resistance of the alloys compared to silicon. This enhanced short-crack response is linked to the fine microstructural size scale of the eutectic structures, which allow toughening mechanisms to be activated during very early stages of crack growth. The range of fracture toughness and wear resistance values measured for the Si-(Cr,V)Si2 alloys elucidates the potential of these materials as viable structural materials in place of powder-processed ceramics.

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3.13b. The load-crack extension data was fitted using a linear function in the regime governed solely by the material’s R-curve behavior (i.e. where the stress intensity function for the chevron-notch geometry produces an increasing elastic strain energy release rate, or more simply, unstable fracture).

Figure 3.19: Schematic of a eutectic colony microstructure which exhibits a random distribution of the reinforcing minor phase orientation as marked by the bold lines or circles (circles represent an orientation into the plane of the page). As a crack propagates through a region low crack resistance region (where the colony is oriented parallel to the crack direction), it is likely to encounter regions of high crack resistance (where the colonies are oriented more perpendicular to the crack direction) before finding another low crack resistance path. This type of microstructure is expected to enhance the isotropy of in-situ toughened Si-(Cr,V)Si$_2$ alloys by ensuring that microstructural toughening mechanisms, such as crack bridging, are activated prior to excessive crack growth.

Figure 3.20: Illustration showing how postponement of the rising R-curve behavior in Si-(Cr,V)Si$_2$ alloys leads to reduced fracture toughness values ($K_{IVb}$) as measured by the CNB method. In this example, the delayed rising R-curve response of alloy X2 compared to an alloy X1 of the same composition is due to the presence of overgrown silicon regions near the notch tip which provide low energy fracture paths. This type of effect is expected to greatly reduce the reliability of Si-(Cr,V)Si$_2$ composites.

Figure 4.1: Ball-on-disk test apparatus used for wear testing of Si and Si-(Cr,V)Si$_2$ composites. (Image reproduced from http://www.csm-instruments.com/en/Tribometer)

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Figure 4.4: The shapes of the coefficient of friction ($\mu$) curves during sliding wear can be identified with an underlying mode of wear for the given testing conditions. (a) At $W = 1$ N, very smooth curves and high values of $\mu$ indicate that adhesive wear mechanisms (characteristic of mild wear) are active at low loads. (b) At $W = 3$ N, the Si-(Cr,V)Si$_2$ alloys display the same smooth curves as in (a) indicating they are still within the mild wear regime. However, the ‘noisy’, undulating curve displayed for Si at this load indicates successive fracturing (peaks) / material removal (valleys) events are taking place. (c) At $W = 6$N, silicon and two of the composite alloys (alloy E and F) are shown to display undulating $\mu$-curves, whereas alloys G and H maintain smooth curves suggesting that large-scale material removal is minimal for the latter two alloys.

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Figure 5.1: Ashby plot of specific fracture toughness ($K_{ic}/\rho$) versus specific strength ($\sigma_f/\rho$). By more than doubling or tripling silicon’s fracture toughness without greatly increasing its density, in-situ toughened Si-(Cr,V)Si\textsubscript{2} composites can achieve specific strength and toughness values within the same range as those displayed by most engineering ceramics.

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all of which are used as tribological components in applications where abrasive wear is a concern. It should be noted that the wear rate constants shown in the plot are given for operating pressures that are a fraction of the maximum bearing pressure \((P/P_{\text{max}})\) for a given material such that \(k_a\) is a true constant (i.e. does not increase with increasing load). The maximum bearing pressure is proportional to the hardness of the material. (Image adapted from [171])

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Chapter 1: How to design an in-situ toughened silicon-rich alloy

1.1 Introduction: Silicon as a basis for structural materials

Being that silicon is the second most abundant element on earth, making up about 25.7% of the earth’s crust [1], it is no surprise that this material has been so extensively studied for a wide variety of applications. In microelectronic devices, as a popular alloying element in aluminum alloys and steels, or even as a constituent in polymeric silicone compounds, silicon has been the major focus of research in a large number of engineering fields and industries. Through such research the properties of silicon have been thoroughly characterized [2-4]. A majority of the properties studied, however, pertain to silicon in its single crystalline form. This is especially true for the mechanical properties, or more specifically, the fracture characteristics of silicon.

It is widely known that at relatively low temperatures (below about half of its melting temperature) silicon is an inherently brittle material due to the nature of its covalent bonding and diamond cubic crystal structure. Perhaps it is for this reason that manufacturers of silicon have rarely considered the possibility of using this material as a major component in structural engineering applications [5]. However, in terms of other physical and mechanical properties, such as its relatively high stiffness (\(E \approx 140 - 165\) GPa), high hardness (\(H \approx 9-11\) GPa), high compressive strength (\(\sigma_f \approx 3200 - 3500\) MPa), and low density (\(\rho = 2.3\) g/cm\(^3\)), silicon exhibits some promise as a structural material. Given lower material and processing costs to produce silicon alloys as compared to many engineering ceramics (i.e. casting versus powder processing), there is also a large potential economic benefit of being able to use cast silicon-based alloys in place of ceramics for some structural applications. One crucial drawback of silicon, however, is its inferior fracture toughness (\(K_{IC} \approx 0.8 -1.0\) MPa·m\(^{1/2}\)) compared to most engineering ceramics (\(K_{IC} \approx 2 - 10\) MPa·m\(^{1/2}\)). As an example of the comparison between the mechanical properties of silicon and some commonly used engineering ceramics, an Ashby chart of the specific fracture toughness (\(K_{IC}/\rho\)) versus specific compressive strength (\(\sigma_f/\rho\)) of materials is shown in Fig. 1.1. Although silicon’s specific strength is among the highest of those displayed by engineering ceramics, its specific fracture toughness is only half of that displayed by engineering ceramics. Through the work of this thesis, it will be shown that the same principles of alloy and
microstructure design used to toughen engineering ceramics can also be used to improve the fracture toughness of silicon via the development of a Si-rich alloy with a composite-like microstructure. By naturally (in-situ) forming such a structure during solidification, these alloys can be produced using much simpler, less expensive casting processes than the powder processing routes typically used to produce engineering ceramics. Studies of the microstructural and mechanical properties of this new class of ‘castable ceramics’ will reveal the potential of Si-rich alloys as structural materials.

Figure 1.1: Ashby plot of specific fracture toughness \( \left( \frac{K_{IC}}{\rho} \right) \) versus specific strength \( \left( \frac{\sigma_f}{\rho} \right) \). Silicon’s high strength and low density make its specific strength one of the highest compared to those displayed by engineering ceramics. However, silicon’s extremely low fracture toughness make its specific toughness only half of that displayed by most engineering ceramics.

The remainder of this chapter will review existing studies of mechanical properties of single- and polycrystalline silicon, as well as of silicon-based intermetallic compounds (specifically the disilicides), and silicon-rich (eutectic-based) alloys (Section 1.2). A summary of the physical, crystallographic, and thermal properties of silicon and its disilicides are presented in Section 1.3. The survey of all such properties from these two sections, in combination with some basic governing principles of engineering composite design, will lay the foundation on which to direct
the selection of a specific material system for designing a castable, silicon-rich (Si > 50 wt. %) alloy that is toughened during (i.e. in-situ) the casting process (Section 1.4). The final section of this chapter (Section 1.5) will describe the overall problem statement and the specific research tasks which compromise the entirety of this thesis.

1.2 Fracture properties of silicon and silicon-based materials

1.2.1 Single- and polycrystalline silicon

The fracture behavior of single crystal silicon has been the subject of numerous studies over about half a century. Some of the first fracture studies [6, 7] were actually performed in efforts to determine the surface energies of simple crystals. Both Gilman [6] and Jaccodine [7] used cleavage experiments in which double cantilever beam specimens were mechanically tested in liquid nitrogen (T = -196 °C) to determine the surface energy of cleavage planes. Using Irwin’s [8] notation of the Griffith [9] fracture theory, these surface energies can be used to determine the fracture toughness of Si for each of the respective cleavage planes, giving values of about 0.65 MPa·m¹/², 0.86 MPa·m¹/², and 0.72 MPa·m¹/² for the S, {100}, and {110} planes.*

Following these initial cleavage studies of single crystalline Si, the development of silicon-based semiconductor devices, and later micro/nanoelectromechanical devices (MEMs/NEMs), sparked the need for more reliable mechanical data of single crystal silicon at various size scales. As a result, a multitude of experimental [10-22] and computational [19, 23] approaches to measuring the fracture properties of this material were developed. Table 1.1 summarizes the experimental and computational methods used in these tests, as well as the resulting fracture toughness values determined for specific fracture planes. Although there is some scatter in the data reported between these works, most of the fracture toughness values lie within the range of about 0.8 – 1.0 MPa·m¹/², with some of the micro and nano-scale tests producing values slightly above this range. In all cases, the authors have found the fracture toughness of single crystal silicon to be highly dependent on the crystallographic orientation, generally citing the {111} cleavage plane

* The conversion of surface energy to fracture toughness was performed for Mode I plane strain fracture toughness assuming that silicon is an ideally brittle solid (i.e. the fracture energy is equal to the reversible surface energy). Elastic constants used in the calculations were $E = 165$ GPa and $\nu = 0.22$. 

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### Table 1.1: Fracture toughness values measured for various forms of single crystalline silicon

<table>
<thead>
<tr>
<th>Specimen Size</th>
<th>Fracture Plane Orientation</th>
<th>Dopant/Resistivity (Ω·cm) or Concentration (atoms·cm⁻³)</th>
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* Test specimen dimensions refer to: macro (d ≥ 1mm); micro (d ≤ 1mm); nano (d ≤ 1µm) where d is smallest specimen dimension

** DCB - double cantilever beam; FPB - four-point bending; SDM - spark discharge method; DTM - double torsion method; MI – micro-indentation; ET - erosion technique; MD - molecular dynamics; OCTM - on-chip tensile testing method; PE-DCB - plasma etched double cantilever beam; AFMBT - atomic force microscope bending test
as having the lowest and \{100\} the highest fracture surface energy (i.e., lowest and highest fracture toughness, respectively). No size scaling effects for the fracture toughness of single crystal silicon have been observed.

Along with single crystalline silicon, the fracture properties of polycrystalline silicon (or polysilicon) have been of engineering interest for a variety of reasons, including the processing of single crystalline silicon or the mechanical integrity of silicon-based devices such as solar cells or MEMs/NEMs. All of these different applications have motivated research on the fracture of polysilicon having microstructures of varying size scale: from the macro- [12, 15, 24, 25] and micro-scale [26-36] down to the nano [37-39] and amorphous [39-44] regimes. Results from all such works (see Table 1.2) have shown the fracture toughness of polycrystalline Si to be in the same range as found for single crystal Si (i.e. 0.8 – 1.0 MPa·m^{1/2}). The fracture toughness of bulk polycrystalline silicon has generally been found to be weakly dependent on its microstructure [24, 25], although Brodie et al. [24] did observe a slight dependence on microstructural morphology; a small increase in $K_{IC}$ was reported when the crack propagated perpendicular to the high aspect ratio dimension. It was also found that for a given strain rate, the brittle-to-ductile transition temperature (BDTT) occurred at higher temperatures for polysilicon specimens as compared to single crystalline Si [24]. Furthermore, the increase in fracture toughness at the BDTT was observed to be much more gradual than the sharp transition normally found for single crystalline Si. These differences were attributed to the impediment of dislocation motion by grain and twin boundaries [24].
1.2.2 Structural disilicides

Refractory-metal silicides, particularly the silicides formed from transition metals in groups IVa-VIa in the periodic table, have been recently gaining more attention as structural materials for high temperature applications [45]. In addition to having high melting temperatures, refractory silicides possess other advantageous material properties such as relatively low densities, high thermal conductivities, high strengths, and reasonable to excellent oxidation resistance [46]. Despite such desirable properties, wide-spread use of structural silicides has been limited by poor toughness at ambient temperatures. As a result, numerous studies have been conducted to understand the deformation mechanisms of silicides in efforts to be able to improve their fracture properties. Of the three most useful classes of silicides (i.e. monosilicides, 5-3 silicides, and disilicides), the mechanical properties of transition metal disilicides (having a stoichiometry of
MSi$_2$, with M being a transition metal) are the most pertinent to the development of a toughened Si-rich alloy since they form eutectic reactions with silicon in the Si-rich regions of M-Si based material systems (see Section 1.4).

Transition metal disilicides can be divided into different groups based on their crystal structures: tetragonal C11b (MoSi$_2$, WSi$_2$), hexagonal C40 (CrSi$_2$, VSi$_2$, NbSi$_2$, TaSi$_2$), orthorhombic C54 (TiSi$_2$), cubic C1 (CoSi$_2$, NiSi$_2$), and orthorhombic C49 (ZrSi$_2$, HfSi$_2$) [47]. Of all the transition metal disilicides, MoSi$_2$ is perhaps the most heavily studied due to its high melting temperature, excellent oxidation resistance, and high strength at elevated temperatures [47]. The mechanical properties of both single crystal [45, 48-51] and polycrystalline [52-55] forms of MoSi$_2$ have been characterized over the past 20 years. The compressive deformability of MoSi$_2$ single crystals has been found to be very orientation dependent. The {011} <100> and the {013} <331> slip systems are operative at room temperature, although the latter is not operative in the [001] orientation at temperatures below 900 °C [45, 56], which is cited as the brittle-to-ductile transition temperature (DBTT) for this material. Small amounts of solid solution substitutions of Al for Si in MoSi$_2$ single crystals to form C11$_b$ Mo(Al,Si)$_2$ has been observed to modify dislocation plasticity by significantly lowering the critical resolved shear stress necessary to activate the {110} $\frac{1}{2}$<111> slip systems at room temperature [48]. However, the presence of Al does not seem to significantly improve the fracture toughness of single crystal MoSi$_2$ [48]. Larger additions of Al (greater than 10 at% Al) in MoSi$_2$ leads to a polymorphic transformation from the C11$_b$- to a C40-type structure and actually decreases the ductility and fracture toughness of Mo(Al,Si)$_2$ compared to its pure single crystalline form [57].

Relatively low DBTT values have been observed for single crystals of VSi$_2$, NbSi$_2$, and VSi$_2$ (all C40-type disilicides) under compression – 200 °C, 400 °C, and 500 °C, respectively [58]. The yield strength at room temperature for these three disilicides was found to be around 400 MPa with deformation only occurring by basal (0001) $<1\overline{2}10>$-slip [59]. Anomalous strengthening of these materials is also found to occur between 1100 and 1400 °C. On the other hand, CrSi$_2$ (the other C40-type disilicide) is not deformable below temperatures of 700 °C and has a negative temperature dependence of yield stress at all temperatures up to its melting point [57, 59, 60]. This difference in mechanical behavior among the C40 disilicides has been attributed to
a change from a conventional shear (VSi$_2$, TaSi$_2$, and NbSi$_2$) to a synchroshear (CrSi$_2$) deformation mechanism [58]. The room temperature elastic properties of single and polycrystalline forms of both C11$_b$ and C40 transitional metal disilicides are given by Chu et al. [61].

Orthorhombic C54 and cubic C1-type disilicide structures have received considerably less attention as potential structural materials for high temperature applications due to their relatively low melting temperatures. The low density of TiSi$_2$, however, has sparked some interest in the characterization of its mechanical properties. Polycrystalline forms of TiSi$_2$ have been reported to deform only above 700 °C though slip on the (001)<110> slip system [62, 63], whereas single crystals are deformable down to room temperature when this slip system is operative [64, 65]. The α-NiSi$_2$ (C1) structure transforms into β-NiSi$_2$ at 981 °C and then undergoes a peritectic reaction at 993 °C in which it transforms into liquid and silicon [45]. Therefore, this material has not been regarded as a viable structural material at elevated temperatures. Consideration of CoSi$_2$ as a structural material has been due to its low density and exceptional oxidation resistance. The primary slip system for CoSi$_2$ is {001} <100>, although polycrystalline forms of this material can only be deformed at temperatures above 500 °C at which secondary slip systems of {111} <110> and {110}<110> become activated [66].

For comparison of the fracture behavior of the various disilicides, Fig. 1.2 displays a compilation of data on the temperature dependence of the critically resolved shear stress (CRSS) for primary slip on those systems which are accessible at low temperatures in disilicide single crystals. For most disilicide single crystals, the primary slip system can be activated at around 200 – 350 MPa. One notable exception seems to be MoSi$_2$, for which a CRSS of about 550 MPa is needed to activate slip on the {011} <100> system (denoted by the black open circle, which has been interpolated from data in [45]). Also, as mentioned previously, no slip is observable in CrSi$_2$ single crystals below 700 °C. The open blue diamond at around 700 °C (CRSS = 718 MPa) is for a CrSi$_2$ single crystal which was observed to fail without any plastic flow [60]. A more detailed account of the mechanical properties of the disilicides can be found in several review articles [45, 47, 67] and the references therein.
Figure 1.2: Temperature dependence of the critically resolved shear stress (CRSS) for primary slip on systems (noted in legend) which are accessible at low temperatures in various disilicide single crystals (as measured in compression). All structures show a negative temperature dependence in their CRSS with some anomalous strengthening at elevated temperatures (except CrSi$_2$ which shows no strengthening). Slip in MoSi$_2$ single crystals requires a noticeably higher CRSS at room temperatures than do other disilicides. Also, no slip is observable in CrSi$_2$ for which failure without plastic flow has been observed to occur at 718 MPa at around 700 °C (open blue diamond). (Data compiled from the following sources: MoSi$_2$ [45] (open circle is interpolated from data); NbSi$_2$, TaSi$_2$ [45]; CrSi$_2$ [45] and [60]; VSi$_2$ [59]; TiSi$_2$ [65]; CoSi$_2$ [66])

One of the major drawbacks of disilicides (especially in their polycrystalline form) as structural materials is their poor fracture toughness at room temperature. As discussed above, this a result of the limited number of slip systems operative at low temperatures. One method to improve the toughness of these materials has been by forming duplex silicides; that is, a dual-phase microstructure composed of different silicide crystal structures. Particular focus has been put on combining the C40, C11$_b$, and C54 structures since all of them have similar atomic arrangements and stacking sequence of atoms on their close packed (dislocation glide) planes [68]. Also, they are in equilibrium with each other in pseudo-binary and pseudo-ternary systems [69] which allows the phases to be formed simultaneously in a lamellar structure during
processing without the presence of additional unwanted phases. Duplex structures have been shown to display improved fracture properties over the individual phases composing the material. For example, Hagihara et al. [70] showed directionally solidified MoSi$_2$ (C11$_b$) / NbSi$_2$ (C40) duplex-phase silicides to have enhanced fracture properties due to the suppression of crack propagation at the lamellar interface between the C11$_b$ and C40 phases (Fig 1.3). A more detailed discussion of the disilicide crystal structures is presented in Section 1.3.

**Figure 1.3:** Vickers indent (1000 gf load) in a MoSi$_2$ (C11$_b$) / NbSi$_2$ (C40) duplex silicide showing crack arrest at the lamellar interface. (Image reproduced from [70])

Besides forming duplex silicides, there are not many other well defined approaches to improving the room temperature fracture toughness of structural disilicides through an in-situ, or alloying method. However, there are microstructural design techniques that have been proven to be successful in the in-situ toughening of monosilicides and 5-3 silicides. One strategy is the formation of in-situ ductile phase-intermetallic composites through eutectic solidification. For instance, the fracture toughness for Ti$_5$Si$_3$ increases from 2 MPa·m$^{1/2}$ in its monolithic state to 12 MPa·m$^{1/2}$ for a two-phase Ti-Ti$_5$Si$_3$ unidirectionally solidified eutectic alloy [69]. Bewlay et al. [71] measured the fracture toughness of alloys made from the V-V$_3$Si and Cr-Cr$_3$Si eutectic systems to be 6-7 times that of pure silicon – 6.8 MPa·m$^{1/2}$ and 7.3 MPa·m$^{1/2}$, respectively [71].
Ductile phase toughening through eutectic reactions has also been the basis for Mo-Si-B [72-74] and Nb-Si [75] alloys being developed to replace Ni-based superalloys in applications such as aerospace engines and power generation.

Due to the fact that there are no known disilicides that form a terminal metal solid solution through eutectic reactions [69], limited work has been done to investigate the mechanical properties of disilicide composites with either 5-3 silicides or silicon itself – the latter tending to form for silicon-rich compositions. Actually, to the author’s present knowledge, the only data gathered for the mechanical properties of silicon-disilicide (Si-MSi₂) eutectic alloys, as well as other silicon-rich alloys, has been through the works of Karl Forwald (see Section 1.2.3). The lack of interest in such materials may be due to the seemingly low potential for these brittle-brittle composites as structural materials, and/or to the relatively lower temperatures at which Si-MSi₂ eutectic reactions occur compared to other silicide-metal eutectic reactions – making them less useful for extremely high temperature applications. Although major improvements in the fracture properties of transition metal disilicides has not yet been achieved, these materials possess a combination of physical, structural, thermal (see Setion 1.3) and mechanical properties that are valuable to the development of a toughened silicon-rich alloy. This will be discussed in more detail in Section 1.4.

### 1.2.3 Silicon-rich (eutectic-based) alloys

One of the most, and perhaps the only, systematic study of the mechanical properties of true Si-rich alloys is that of Karl Forwald et al. [5, 76, 77]. In 1997, Forwald published his doctoral dissertation [5] entitled ‘Properties of some silicon rich alloys’. His work, which was funded by Elkem ASA®, was based on a project called “New Silicon Alloys” and attempted to explore the potential applications and markets for MG-Si based structural materials. Forwald studied both the microstructural [76, 77] and mechanical properties of binary and ternary Si-rich alloys containing various amounts of Al, Cu, V, Co, Ti, as well as minor additions of P, B, and Sr [5]. The alloys were produced by vacuum induction melting and subsequent casting into copper molds. Rapid solidification of the alloy was performed by induction and arc melt-spinning processes [5]. In addition to the as-cast alloys, some of the rapidly solidified materials were hot pressed prior to characterization. Forwald evaluated properties such as density, Young’s
modulus, stiffness to density ratio, compressive strength, Vickers hardness, corrosion resistance, and also estimated the fracture toughness.

In general, Forwald noted that the Si-rich alloys were brittle, exhibiting transgranular fracture [76] and negligible plasticity under compressive loading conditions [5]. However, Si-Al with Al contents in excess of 20 % did display plastic deformation during compression testing [5]. Fracture toughness estimations were all obtained using a Vickers microindentation technique. Since the area probed by indentation is much smaller than microstructural features of the alloys being tested, fracture toughness values were mostly reported for individual phases or regions, and not as global measurements for entire alloy microstructure (with some exceptions). Some noteworthy toughness values measured for the Si-rich alloys studied include:

- Eutectic Si-VSi2 in a cast Si-7V (wt. %) alloy (1.6 MPa·m$^{1/2}$)
- CoSi2 grains in cast Si-Co alloys with Si contents between 44 – 56 wt. % Si (1.5 – 3 MPa·m$^{1/2}$)
- Melt-spun Si-51Co-0.9Sr (wt. %) alloy (3.6 MPa·m$^{1/2}$ macro fracture toughness)
- Cast Si-20Co-28Ti-0.2B (wt. %) alloy (2.8 MPa·m$^{1/2}$ macro fracture toughness)

The fracture toughness of the Si grains in the cast or melt spun materials was not modified by alloying, and remained around 1.0 MPa·m$^{1/2}$ for all the compositions studied. Powder metallurgical processing was not found to improve the mechanical properties of the binary Si-rich alloys, but did increase the fracture strength of ternary alloys [5]. Thus far, no known attempts have been made to perform large scale testing (i.e. pre-cracked four point bend tests, plane strain $K_{ic}$ tests, etc.) in order to measure macro fracture toughness values of these Si-rich alloys, or in some cases, validate the reported macro fracture toughness values measured by microindentation. Nevertheless, Forwald’s results provide a direction along which the materials selection process in the development of toughened Si-rich alloys may proceed.
1.3 Physical, structural, and thermal properties of silicon and disilicides

In the development of an in-situ toughened Si-rich alloy, there are other important material properties to consider than just the mechanical behavior of the individual constituents. For example, in order to preserve the advantageous low density of Si ($\rho = 2.3 \text{ g/cm}^3$) in a cast Si-rich composite, it is favorable to alloy Si with a metal which forms another low density phase during solidification (in this case, a low density disilicide). In terms of crystal structure, pseudo-binary and pseudo-ternary diagrams [69, 78, 79] between some of the different disilicide structural groups can be used to predict the stability of these phases when combined with one another. A more detailed description of such diagrams will be presented here since they allow one to more easily control the microstructure of cast Si-rich alloys. Finally, toughening mechanisms in composite materials, especially in brittle-brittle composites, are strongly governed by the interfacial properties between the matrix and reinforcing phase. These interfacial properties are affected by residual stresses which arise from the differences in thermal expansion (as well as elastic properties) between the matrix and reinforcing phase as the composite is solidified during processing (a more detailed review of toughening mechanisms is presented in Section 1.4). Therefore, knowledge of the thermal expansion properties of the alloy components is crucial in optimizing the fracture resistance of the composite microstructure. This section presents a summary of the physical, structural, and thermal properties of the more popular and well-studied structural disilicides (i.e. those discussed in Section 1.2). A much more comprehensive review of the various properties of all types of silicides is given by Goldschmidt [80].

1.3.1 Physical and structural data

Density and crystal structure data for silicon and some common structural disilicides are listed in Table 1.3. The crystal structures, which are illustrated in Fig. 1.4 for the disilicides, are listed by their Strukturbericht designation. From Table 1.3, it is seen that the C54, C1, and two C40 disilicides (VSi$_2$ and CrSi$_2$) have relatively low densities compared to those displayed by the C11$_b$ disilicides and the other two C40 disilicides (NbSi$_2$ and TaSi$_2$). As mentioned in Section 1.2, the C11$_b$, C40, and C54 structures (Fig. 1.4 a-c) are all related by a difference in their atomic stacking sequence. In all three crystal structures, the transition metal layers are pseudo-hexagonally arranged so that a transition metal atom (M) is coordinated by six Si atoms, whereas
A Si atom is coordinated by three M atoms and three Si atoms (Fig. 1.5a) [81]. The sites labeled A-D in Fig. 1.5a represent equivalent positions for stacking the MSi₂ layers if the stacking is performed such that the M atoms occupy saddle positions directly above Si-Si bonds [81]. The close packed planes are the (110), (0001), and (001) for the C11b, C40, and C54 structures, respectively, and all have similar atomic arrangements except for a slight lattice distortion [68] (Fig. 1.5b). The C11b, C40, and C54 structures are formed through AB, ABC, and ADCB atomic stacking of the atoms on the closed packed planes (where again A, B, C, D refer to the transition metal sites in Fig. 1.5a), as shown in Fig. 1.5b. For the C40-type structures, the stacking can also be ABDABD (known as the P6₄22 space group) instead of the ABCABC (known as the P6₂22 space group) stacking shown in Fig. 1.4a and 1.5b. Of the C40-type disilicides, VSi₂, CrSi₂, and TaSi₂ have been determined to belong to the P6₄22 space group and NbSi₂ to the P6₂22 space group [82].

Table 1.3: Physical and structural data of silicon and some common structural disilicides

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystal Structure</th>
<th>Lattice parameters (nm)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>A4 (Diamond cubic)</td>
<td>a = 0.543; b = a; c = a [83]</td>
<td>2.33</td>
</tr>
<tr>
<td>MoSi₂</td>
<td>C11b (tetragonal)</td>
<td>a = 0.321; b = a; c = 0.785 [84]</td>
<td>6.20 [80]</td>
</tr>
<tr>
<td>WSi₂</td>
<td>C11b (tetragonal)</td>
<td>a = 0.321; b = a; c = 0.783 [84]</td>
<td>9.86 [47]</td>
</tr>
<tr>
<td>VSi₂</td>
<td>C40 (hexagonal)</td>
<td>a = 0.457; b = a; c = 0.637 [84]</td>
<td>4.66 [61]</td>
</tr>
<tr>
<td>NbSi₂</td>
<td>C40 (hexagonal)</td>
<td>a = 0.480; b = a; c = 0.659 [84]</td>
<td>5.70 [61]</td>
</tr>
<tr>
<td>TaSi₂</td>
<td>C40 (hexagonal)</td>
<td>a = 0.478; b = a; c = 0.657 [84]</td>
<td>9.21 [61]</td>
</tr>
<tr>
<td>CrSi₂</td>
<td>C40 (hexagonal)</td>
<td>a = 0.443; b = a; c = 0.637 [84]</td>
<td>5.02 [61]</td>
</tr>
<tr>
<td>TiSi₂</td>
<td>C54 (orthorhombic)</td>
<td>a = 0.827; b = 0.480; c = 0.855 [84]</td>
<td>4.39 [47]</td>
</tr>
<tr>
<td>CoSi₂</td>
<td>C1 (cubic)</td>
<td>a = 0.537; b = a; c = a [80]</td>
<td>4.95 [47]</td>
</tr>
</tbody>
</table>
Figure 1.4: Hard-sphere models of crystal structures for common structural disilicides. Identification of the atom type in each structure is shown at the top right atom and is designated as either M (transition metal) or Si (silicon). (Images (a), (b), and (d) reproduced from [47] and (c) reproduced from [85])

Figure 1.5: (a) Atomic arrangement of transition metal layers (MSi$_2$) found in many structural disilicides. These layers correspond to the (110), (0001), and (001) planes for C11$_b$, C40, and C54 structures, respectively. (b) Stacking sequence of atoms on close packed planes according the transition metal layer sites shown in (a). (Images reproduced from [68])
The similar nature of the atomic arrangements in the C11b, C40, and C54-type disilicides leads to a limited solubility between the different structures. Pseudo-binary ASi2-BSi2 phase diagrams (Fig. 1.6) [78] have been determined for different pairs of disilicides and allow one to determine the phase stability of a specific disilicide structure relative to a different, competing structure. In Fig. 1.6, the different markings represent compositional regions in which a single disilicide structure exists. The white areas are compositional regions in which two different phases (or structures) of disilicides are in equilibrium with one another. These diagrams show that the C40 structure tends to display the largest regions of stability, or in other words, have a larger solubility for the other elements. Also, according to these diagrams, the C40-type disilicides are all completely soluble in one another (as noted by no white areas). It is thus obvious that the C40 structure displays the most opportunity for alloying [69]. The cubic C1-type disilicide structure (Fig. 1.4d) bears no crystallographic similarities to the other structures, and thus has limited alloying opportunities [69].

![Figure 1.6: Schematic of ASi2-BSi2 pseudo-binary diagrams between different transition metals disilicides (where A and B represent the different transition metals listed in this table). Compositional regions of stability for the single disilicide structures are shown by different markings, whereas regions of two-phase equilibrium (i.e. no single stable phase) are shown by the white regions. (Image adapted from [81] which is based on data published in [78])](image)

1.3.2 Thermal expansion data

An interest in the thermal expansion properties of transition metal disilicides has mainly been due to the use of these materials in the microelectronics industry. However, as will be shown in Section 1.4, these properties will also play a crucial role in governing the fracture properties of
in-situ Si-rich composites based on Si-MSi$_2$ eutectic reactions. Most transition metal disilicides display anisotropic thermal expansion properties, as should be expected by their non-cubic crystal structures (Fig. 1.4). The only exception to this, of course, is for the cubic C1-type disilicides. Table 1.4 gives the temperature-dependent linear and volumetric thermal expansions found for silicon and structural disilicides. The linear expansions of the disilicides are all larger

**Table 1.4:** Linear and volumetric thermal expansion coefficients for silicon and structural disilicides

<table>
<thead>
<tr>
<th>Substance</th>
<th>Linear ($\alpha_{a,b,c}$) and volumetric ($\alpha_V$) thermal expansions (K$^{-1}$)</th>
<th>Temperature range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>$\alpha_a = (3.725[1 - \exp[-5.88 \times 10^{-3}(T - 124)] + 5.548 \times 10^{-4}T]) \times 10^{-6}$ [83] $\alpha_V \approx 3 \cdot \alpha_a$</td>
<td>300 - 1500</td>
</tr>
<tr>
<td>MoSi$_2$</td>
<td>$\alpha_a = 5.617 \times 10^{-6} + 3.544 \times 10^{-9}T$ $\alpha_c = 4.115 \times 10^{-6} + 5.565 \times 10^{-9}T$ $\alpha_V = 1.530 \times 10^{-5} + 1.268 \times 10^{-8}T$</td>
<td>(all values from [86]) 300 - 1400</td>
</tr>
<tr>
<td>WSi$_2$</td>
<td>$\alpha_a = 6.512 \times 10^{-6} + 2.513 \times 10^{-9}T$ $\alpha_c = 8.800 \times 10^{-6} + 2.404 \times 10^{-9}T$ $\alpha_V = 2.200 \times 10^{-5} + 7.254 \times 10^{-8}T$</td>
<td>(all values from [86]) 300 - 1400</td>
</tr>
<tr>
<td>VSi$_2$</td>
<td>$\alpha_a = 8.016 \times 10^{-6} + 4.598 \times 10^{-9}T$ $\alpha_c = 7.485 \times 10^{-6} + 4.865 \times 10^{-9}T$ $\alpha_V = 2.344 \times 10^{-5} + 1.410 \times 10^{-8}T$</td>
<td>(all values from [86]) 300 - 1400</td>
</tr>
<tr>
<td>NbSi$_2$</td>
<td>$\alpha_a = 9.078 \times 10^{-6} + 5.738 \times 10^{-10}T$ $\alpha_c = 8.653 \times 10^{-6} + 2.060 \times 10^{-9}T$ $\alpha_V = 2.422 \times 10^{-5} + 6.663 \times 10^{-8}T$</td>
<td>(all values from [86]) 300 - 1400</td>
</tr>
<tr>
<td>TaSi$_2$</td>
<td>$\alpha_a = 6.783 \times 10^{-6} + 4.116 \times 10^{-9}T$ $\alpha_c = 6.127 \times 10^{-6} + 5.672 \times 10^{-9}T$ $\alpha_V = 1.967 \times 10^{-5} + 1.390 \times 10^{-8}T$</td>
<td>(all values from [86]) 300 - 1400</td>
</tr>
<tr>
<td>CrSi$_2$</td>
<td>$\alpha_a = 8.177 \times 10^{-6} + 9.903 \times 10^{-9}T$ $\alpha_c = 8.986 \times 10^{-6} + 7.617 \times 10^{-10}T$ $\alpha_V = 2.530 \times 10^{-5} + 2.055 \times 10^{-8}T$</td>
<td>(all values from [86]) 300 - 1400</td>
</tr>
<tr>
<td>TiSi$_2$</td>
<td>$\alpha_a = 6.875 \times 10^{-6} + 7.262 \times 10^{-9}T$ $\alpha_b = 6.925 \times 10^{-6} + 6.344 \times 10^{-9}T$ $\alpha_c = 5.409 \times 10^{-6} + 8.196 \times 10^{-9}T$ $\alpha_V = 1.889 \times 10^{-5} + 2.212 \times 10^{-8}T$</td>
<td>(all values from [86]) 300 - 1400</td>
</tr>
<tr>
<td>CoSi$_2$</td>
<td>$\alpha_a = 14.2 \pm 0.4 \times 10^{-6}$ [87] $\alpha_V \approx 3 \cdot \alpha_a$</td>
<td>400 - 1050</td>
</tr>
</tbody>
</table>
than those of silicon for the temperature ranges given. This will prove to be advantageous in controlling the interfacial properties of Si-MSi$_2$ based composite materials (Section 1.4). It is also interesting to note that silicon also undergoes a volume expansion (~10%) upon freezing. During casting of silicon, expansion against the mold walls can induce stresses which crack the material during solidification. Disilicides, on the other hand, shrink upon solidifying. This suggests that there is an opportunity to minimize or eliminate expansion / shrinkage of cast Si-MSi$_2$ based composites by controlling the amount of each phase present in the microstructure.

1.4 Application of composite design theory to silicon-disilicide eutectic systems

Ceramics, similar to silicon, are inherently brittle in their natural (as-pressed) state. Advancements in the toughening of engineering ceramics, however, have led to a fundamental understanding of the mechanics which govern the fracture response of these materials. Therefore, in selecting an optimal materials system to develop a castable, in-situ toughened Si-rich alloy, it is pertinent to consider the microstructural design techniques that have been implemented in improving the fracture properties of engineering ceramics. Section 1.4.1 will describe some toughening mechanisms that have been achieved in both artificially and naturally reinforced ceramic-matrix (i.e. brittle-brittle) composites. An appreciation for the effect of the constituent material properties on the macroscopic fracture properties of brittle-brittle composites will elucidate the potential of Si-MSi$_2$ eutectic composites to achieve similar toughening responses. Section 1.4.2 will discuss the advantages of using disilicide-based eutectics in the development of Si-rich composites compared to other Si-based eutectic systems. In addition, the different Si-MSi$_2$ eutectic systems will be compared with one another on the basis of their capability to induce microstructural toughening during a casting process. From this analysis, a specific Si-based materials system is chosen for further study in this thesis work, the specific objectives of which are described in Section 1.5.

1.4.1 Toughening in brittle-brittle composites

Toughening mechanisms in ceramics are generally classified into one of the following groups according to the type of microstructure-crack interaction: crack-tip interactions, crack bridging, and crack tip shielding. Only the first two types of mechanisms will be discussed here since (as
will be shown in the next section) they have a direct application in the development of toughened Si-rich alloys.

For toughening mechanisms based on crack-tip interactions, the path of a propagating crack is impeded by the presence of obstacles that can take the form of second-phase particles, fibers, or whiskers. One type of crack-tip interaction, known as crack deflection, is based on the formation of a non-planar crack (post deflection) that is subjected to a lower stress intensity than the original planar crack (prior to deflection) that existed in pure mode I (tensile) loading. The non-planar crack arises from residual strains present in the material (due to elastic modulus and/or thermal expansion mismatch between the matrix and reinforcement phase) or from the presence of weak interfaces [88]. Using a fracture mechanics approach, Faber and Evans developed a model [88] to predict the amount of toughening that can be achieved solely by the tilting and twisting of the crack about an axis parallel and perpendicular, respectively, to the crack front. It was found that the toughening arises primarily from the twisting of the crack, and that the degree of toughening depends only on the shape and volume fraction of the reinforcing phase (Fig. 1.7). Crack deflection has been estimated to theoretically increase the composite toughness 2-4 times [89] or less [90] than that of the matrix material.
Figure 1.7: Effect of volume fraction and reinforcing particle shape on the degree of toughening achieved by the crack deflection mechanism. (a) The relative crack resistance force of the composite ($G_C$) compared to the matrix ($G_M$) is increased for increasing volume fractions of second phase particles. Also, for a given volume fraction of particles, the effectiveness of toughening is greatest for rod shaped (elongated) particles and least for sphere shaped. (b) Increasing the aspect ratio of elongated particles, such as rods, leads to an increase in the relative toughening achieved by crack deflection. (Images reproduced from [91] which is based on data published in [88])

During crack deflection, a crack can by-pass an obstacle in such a way that it leaves the obstacle intact, for example, by propagating along the interface between the matrix and particle. In this case, the obstacle will be left behind as a ligament in the wake of the crack tip, making it harder to open the crack at a given applied stress [91]. This type of toughening mechanism is called crack bridging and has been observed extensively in whisker-reinforced ceramics, along with ceramics reinforced with second-phase platelets [92, 93] and other particulate phases [94]. Crack bridging has also been achieved through frictional grain pullout in ceramics containing elongated matrix grains [95-100]. Grain bridging is much more prevalent in noncubic materials that exhibit anisotropy in their thermal expansion properties [101]. The role of the matrix, reinforcing phase, and interfaces in governing such crack-bridging processes has been analyzed through micromechanics models of bridging in composites with discontinuous elastic reinforcing ligaments. These models, which will now be presented, have been developed and reviewed in detail in [102] and the references therein. In the present discussion, the models discussed assume
no interfacial friction between the matrix and reinforcing ligament. This is an appropriate assumption when the thermal expansion coefficient of the ligament \( (\alpha_l) \) is greater than that of the matrix \( (\alpha_m) \) – which is the case for composites containing a Si-MSi₂ eutectic microstructure (i.e. \( \alpha_{MSi} > \alpha_{Si} \) as discussed in Section 1.3.2).

The contribution of crack-bridging to the overall toughness of the composite \( (K_{IC}^c) \) is given by:

\[
K_{IC}^c = \left[ E_c \left( J^m + \Delta J^{eb} \right) \right]^{1/2}
\]

(1.1)

where \( E_c \) is the Young’s modulus of the composite, \( J^m \) is the elastic energy change associated with crack extension in the matrix, and \( \Delta J^{eb} \) is the elastic energy change associated with the elastic bridging process assuming no interfacial friction (the ‘J’ specifies that these quantities are determined using the J-integral approach). For cubic materials (such as silicon) that do not display anisotropic thermal expansion properties, matrix toughening by grain bridging would not be expected to play a large role in toughening of the composite, and so \( J^m \) may be expected to be constant for these materials. Thus, improvements the fracture toughness of composites that do not display matrix toughening must come solely from the bridging process of the reinforcement phase.

The energy change associated with the elastic bridging process is defined as:

\[
\Delta J^{eb} = \int_0^{u_{max}} T_u du
\]

(1.2)

where \( T_u \) is the bridging traction, or closure stress, of the ligaments on the crack and \( u_{max} \) is the maximum opening displacement at the end of the bridging zone.

Figure 1.8a shows an illustration of the crack-opening displacement associated with the bridging of a crack by a partially debonded second phase particle. In the absence of interfacial friction,
the maximum crack opening displacement, \( u_{\text{max}} \) (Eq. 1.3), is determined by the strain to failure of the ligament (\( \varepsilon'_f \), Eq.1.4) and the debond length of the matrix-ligament interface (\( l_{db} \), Eq. 1.5) as given in [103]. In Eq. 1.4, \( \sigma'_f \) and \( E_i \) are the fracture strength and Young’s modulus of the reinforcing phase. The term \( \gamma'/\gamma' \) in Eq. 1.5 represents the ratio of the fracture energy of the bridging ligament to that of the reinforcement-matrix interfaces and \( r \) is the radius of the ligament.

\[
\begin{align*}
  u_{\text{max}} &= \varepsilon'_f l_{db} \\
  \varepsilon'_f &= \frac{\sigma'_f}{E_i} \\
  l_{db} &= \frac{r \gamma'}{6 \gamma'}
\end{align*}
\]  

(1.3)  
(1.4)  
(1.5)

**Figure 1.8:** (a) The crack opening displacement of a material reinforced with a discontinuous elastic second phase is controlled by the elastic properties of the reinforcement as well as the interfacial properties between the matrix and reinforcing phase. (b) Bridging traction (T) versus distance behind the crack tip (x) for reinforcement with a discontinuous elastic (brittle) ligament experiencing no interfacial friction with matrix. (Image (a) and inset image in (b) reproduced from [102])
For bridging with no interfacial stresses, $T_u$ will increase linearly with distance behind the crack tip ($x$) until it reaches a maximum ($x_{final}$) at the end of the bridging zone, at which point it immediately drops to zero (Fig. 1.8 b). In this case, the total elastic strain energy associated with the bridging process (Eq. 1.2) can be estimated as Eq. 1.6, with $T_{\text{max}}$ being the product of the ligament fracture stress and the cross-sectional area fraction of the ligaments ($A^{el}$) over which that stress acts (i.e. the area intercepting the crack plane), which is approximately equal to the volume fraction ($V^{el}$) if the ligaments have very large aspect ratios (Eq. 1.7). For uniaxially aligned reinforcements perpendicular to the crack plane, $V^{el}$ will simply be equal to the volume fraction of the reinforcing phase.

$$\Delta J^{eb} = \frac{T_{\text{max}} u_{\text{max}}}{2}$$  \hspace{1cm} (1.6)

$$T_{\text{max}} = \sigma_f A^{el} \approx \sigma_f V^{el}$$  \hspace{1cm} (1.7)

Taking Eqs. 1.3-1.7 and introducing them back into Eq. 1.1 gives the contribution of crack-bridging on the overall toughness of the composite (assuming no frictional pullout, negligible matrix toughening, and high aspect ratio ligaments):

$$K_{lc}^{c} = \left[ E^{c} J^{m} + V^{el} \frac{\sigma_f^{l}}{12E^{l}} \frac{r^{y^{l}}}{\gamma^{l}} \right]^{1/2}$$  \hspace{1cm} (1.8)

Based on Eq. 1.8, there are a few different parameters that one must control in order to maximize the toughening due to fiber bridging. First, the volume fraction of high-aspect ratio reinforcements intercepting the crack plane should be maximized. Ideally, one would like to orient the all reinforcing ligaments perpendicular to the crack plane so that they all contribute to the bridging process. However, in most cases, there will be some degree of randomness in the orientation distribution. This is especially true for most casting processes, except for those that implement directional solidification techniques. Secondly, the reinforcing ligaments should have high fracture strengths. Also, given a specific matrix material, the ratio of ($E^{c} / E^{l}$) should be
maximized, which can be designed for by assuming $E^c$ to be given by a rule of mixtures (this will be made clear in Section 1.4.2). Increasing the radius of the ligaments also increases the toughening due to bridging. Finally, and perhaps most importantly, one must allow for significant debonding of the ligament from the matrix to occur so as to promote large crack opening displacements. This is accomplished by ensuring weak reinforcement-matrix interfaces where $\gamma_i^t<\gamma^t$. Weak interfaces can arise, for example, by residual tensile stresses which are induced during processing (Section 1.4.2). During crack extension in composites exhibiting crack bridging, a rising crack resistance curve (R-curve) may be expected. In materials exhibiting rising R-curve behavior, the apparent toughness increases with increasing crack length due to the growth of the bridging zone with crack extension (Fig. 1.9). However, the bridging zone is expected to reach a limiting size at which point it moves in conjunction with the crack tip [91, 104] and a steady state toughness is reached.

![Figure 1.9: R-curve behavior for alumina matrix composites reinforced with various volume fractions of SiC whiskers. The rising slope of the R-curve and the final (steady state) fracture toughness of the composites increase as the volume fraction of SiC reinforcements increase. This is due to an increase in the bridging zone size, and thus, a larger contribution to crack opening displacement by the fiber reinforcements. (Image reproduced from [94])](image-url)
1.4.2 Achieving microstructural toughening in silicon-based eutectic alloys

From the analysis provided in the previous section, it should be clear that it is imperative to achieve toughening mechanisms such as crack deflection and crack bridging in Si-rich alloys to attain specific fracture toughness values similar to those displayed by engineering ceramics (Fig. 1.1). As mentioned previously, silicon’s cubic crystal structure, and thus isotropic thermal expansion properties, make it difficult to achieve toughening in this material solely by alteration of its microstructure. This fact is suggested by the consistently low fracture toughness values observed in different grain size polycrystalline Si samples (Table 1.2). Thus, microstructural toughening must be achieved by addition of a second reinforcing phase. In designing castable Si-based composites, this phase will be produced through invariant reactions, such as eutectic reactions, that occur during solidification. In the first part of this section, an argument for the use of transition metal disilicides as the reinforcing phase (through eutectic solidification) in Si-rich alloys will be made. Then, in the second part of this section, the various silicon-disilicide eutectic systems will be analyzed in terms of their abilities to promote microstructural toughening via the mechanisms discussed in Section 1.4.1. In the third part of this section, a specific material system is chosen as the focus of study in the remainder of this thesis work.

1) Basis for disilicide phases as reinforcements in Si-rich composites

In Section 1.4.1, an emphasis was put on controlling the composite microstructure so as to maximize the degree of crack interaction with the reinforcements (i.e. either by deflecting around the reinforcement or by bridging resulting from delamination at the matrix-reinforcement interface). For in-situ, eutectic-based reinforced composites, the microstructure can be predicted by the relevant equilibrium phase diagrams. Figure 1.10 identifies the types of eutectic reactions that occur in the Si-rich region of silicon-based binary phase diagrams. The elements marked in red are those that do not form any eutectics on the Si-rich side of the binary system, but rather form a single eutectic in the Si-poor region of the phase diagram. The transition metals highlighted in blue and green all form Si-rich eutectics between a silicide phase and silicon in the Si-rich portion of their respective binary phase diagrams. The metals marked in blue are those that form the disilicides which were previously characterized in Sections 1.2.2 and 1.3. Those metals marked in green form Si-rich silicides that do not have a 1:2 atomic ratio between the
transition metal and silicon (as in the disilicide structure). Many of the elements, which are not highlighted, were not considered as potential alloying constituents for various reasons which are listed below along with some examples:

- High cost: Au, Ag, Pt, Pd, Ir, Rh, Os, Ru, lanthanides, actinides
- Toxicity: Pb, Hg, Cd, Be
- Poor processability (in terms of casting): H, C, N, O, Group VIIA, inert gases
- Lack of thermodynamic data for Si-X system: Na, K

**Figure 1.10:** Periodic table highlighting the different types of binary Si-X eutectic reactions that occur in the Si-rich region of the respective phase diagrams, where X is the alloying element. The red elements do not form any eutectics in the Si-rich region of the Si-X binary phase diagram, whereas the blue and green elements (transition metals) all form silicide-silicon eutectics in the Si-rich region of the Si-X binary phase diagram.
Based on the different types of eutectics formed with silicon, a comparison can be made between the various Si-X binary systems on their potential for microstructural toughening. The binary Si-Al system (Figure 1.11a) is an example of a system in which only a single, Si-poor eutectic composition exists over the entire composition range (i.e. those marked in red in Fig. 1.10). During solidification of an alloy with an initial Si-rich composition (marked on phase diagram in Fig. 1.11a), a large degree of primary silicon solidification takes place prior to eutectic formation. A typical microstructure resulting from such a solidification sequence will be composed of large silicon grains surrounded by regions of the eutectic microstructure (as is shown in Fig. 1.11b for a Si-42Al (wt. %) alloy [5]). Large primary silicon grains in the microstructure allow for regions with no crack-reinforcement interactions, and thus provide paths for easy crack propagation. Therefore, primary Si solidification is expected to be detrimental to the overall toughness of the composite material. To eliminate the presence of primary Si grains, and thus maximize the amount of crack-reinforcement interaction, it is thus preferable to use a system in which a eutectic reaction occurs at a Si-rich composition (i.e. those marked in blue and green in Fig. 1.10). An example of this is shown for the Si-Ti system (Fig. 1.11c), where the Si-TiSi₂ eutectic is formed at a composition of 84 at. % Si (~ 75 wt. % Si). A microstructure of a directionally solidified Si-TiSi₂ eutectic alloy [105] (Fig. 1.11d) reveals a fully eutectic microstructure with a much finer, more homogenous distribution of the Si and TiSi₂ phases than the structure shown in Fig. 1.11b for the Si-42Al (wt. %) alloy. This type of microstructure, which has also been observed for other directionally solidified [105-109] and cast [110] Si-MSi₂ alloys, is optimal for the toughening of silicon due to the absence of large primary silicon grains. It is for this reason that only silicon-silicide eutectic systems were considered for designing a toughened Si-rich alloy. Due to the lack of useful property data for the less commonly studied non-stoichiometric silicides (i.e. those marked in green in Fig. 1.10), however, the present thesis focuses on the use of disilicides as the reinforcing phase in Si-rich alloys.
Figure 1.11: (a) The binary phase diagram for the Si-Al system is an example of a Si-X system in which a single Si-poor eutectic occurs over the entire composition range (in this case at 12.6 wt. % Si). During solidification of an alloy with a Si-rich composition, solidification through the primary Si region results in the formation of large primary silicon grains which degrade the fracture properties of the alloy, as shown in (b) for a Si-42Al (wt. %) alloy. (c) The binary phase diagram for the Si-Ti system is an example of a Si-X system in which a eutectic reaction occurs in the Si-rich region of the phase diagram (in this case at ~75 wt. % Si) to form a silicon-silicide fully eutectic microstructure, as shown in (d) for Si-TiSi₂. Microstructural toughening is expected to occur in such a material due to the absence of large silicon grains and the homogenous distribution of the reinforcing phase (TiSi₂) which maximizes the amount of crack-reinforcement interactions. (Phase diagrams reproduced from [111] which are based on data from [109] and [112] for the Si-Al and Si-Ti systems, respectively. Micrograph (b) was reproduced from [5] and (d) from [105]).
II) Assessment of silicon-disilicide systems in terms of criteria for microstructural toughening

A) Volume fraction of disilicide phase

The first criterion that will be analyzed is the resulting volume fraction of disilicide phase which is formed through the various Si-MSi$_2$ eutectic reactions upon solidification. The volume fraction of reinforcements affects the degree of toughening due to both crack deflection (Fig. 1.7) and bridging (Eqs. 1.7 and 1.8). Table 1.5 lists the eutectic reactions (along with the eutectic temperature, $T_e$) which occur for all the commonly studied structural disilicides discussed in the previous sections [113]. The compositions of the eutectic liquid (which is the same as the global composition of the alloy), as well as the two terminal phases, are given in terms of the amount of silicon in each phase (wt. % Si). The volume fraction of the reinforcing disilicide phase which forms through the given eutectic reactions can be calculated by the tie line rule as:

$$\text{Volume Fraction } MSi_2 = \frac{C_{Si} - C_L}{C_{Si} - C_{MSi_2}}$$

(1.9)

<table>
<thead>
<tr>
<th>Eutectic Reaction</th>
<th>Composition of terminal phases (wt. % Si)</th>
<th>Composition of eutectic liquid, L (wt. % Si)</th>
<th>Volume fraction $MSi_2$</th>
<th>$T_e$ (° C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L \rightarrow Si + MoSi_2$</td>
<td>100 37</td>
<td>93.5</td>
<td>0.103</td>
<td>1400</td>
</tr>
<tr>
<td>$L \rightarrow Si + WSi_2$</td>
<td>100 23.4</td>
<td>93.8</td>
<td>0.081</td>
<td>1390</td>
</tr>
<tr>
<td>$L \rightarrow Si + VSi_2$</td>
<td>100 52.5</td>
<td>94.7</td>
<td>0.112</td>
<td>1400</td>
</tr>
<tr>
<td>$L \rightarrow Si + NbSi_2$</td>
<td>100 37.7</td>
<td>93.7</td>
<td>0.101</td>
<td>1395</td>
</tr>
<tr>
<td>$L \rightarrow Si + TaSi_2$</td>
<td>100 23.7</td>
<td>80.6</td>
<td>0.254</td>
<td>1395</td>
</tr>
<tr>
<td>$L \rightarrow Si + CrSi_2$</td>
<td>100 52.9</td>
<td>78.3</td>
<td>0.461</td>
<td>1335</td>
</tr>
<tr>
<td>$L \rightarrow Si + TiSi_2$</td>
<td>100 54.0</td>
<td>75.5</td>
<td>0.533</td>
<td>1330</td>
</tr>
<tr>
<td>$L \rightarrow Si + CoSi_2$</td>
<td>100 48.8</td>
<td>62.1</td>
<td>0.740</td>
<td>1259</td>
</tr>
</tbody>
</table>
where $C_{Si}$, $C_{L}$, and $C_{MSi_2}$ are the compositions of the silicon (≈ 100 wt. % Si), liquid, and disilicide phase as given in Table 1.5 for each reaction. From these calculations it is shown that only the Si-TaSi$_2$, Si-CrSi$_2$, Si-TiSi$_2$, and Si-CoSi$_2$ eutectic reactions produce disilicide phase in excess of 0.20 volume fraction, which is generally the fraction of reinforcements necessary to achieve substantial toughening in brittle-brittle composites by the crack deflection and bridging mechanisms (see Figs. 1.7 and 1.9 as examples). These systems do however require greater amounts of the alloying additions as noted by the lower Si contents in their eutectic liquid composition.

**B) Elastic properties of constituent phases**

Using the volume fraction data in Table 1.5, an upper-bound composite modulus ($E^c$) can be calculated using a rule of mixtures:

\[
E^c = V_f^{MSi_2} E^{MSi_2} + V_f^{Si} E^{Si} = V_f^{MSi_2} E^{MSi_2} + (1 - V_f^{MSi_2}) E^{Si} \quad (1.10)
\]

where $V_f^{MSi_2}$, $E^{MSi_2}$, $V_f^{Si}$, and $E^{Si}$ are the volume fractions and Young’s moduli (isotropic) of the disilicide phase and silicon, respectively. Young’s moduli data for the disilicides and calculated values of the composite moduli for each of the Si-MSi$_2$ eutectic alloys is given in Table 1.6. From these values, the ratios of $E^c / E^{MSi_2}$ (which represent the term $(E^c / E^l)$ in Eq. 1.8) are determined for each alloy (using $E^{Si} = 150$ GPa). Comparing the data in Tables 1.5 and 1.6, it is shown that the same eutectic systems that maximize the volume fraction of reinforcing phase also tend to maximize the $E^c / E^l$ ratio – a characteristic which should lead to enhanced toughness in these alloys.
Table 1.6: Young’s modulus of disilicides ($E^{MSi_2}$) and their respective Si-MSi$_2$ eutectic alloys ($E^c$)

<table>
<thead>
<tr>
<th>Eutectic Alloy</th>
<th>$E^{MSi_2}$ (GPa)</th>
<th>$E^c$ (GPa)</th>
<th>$E^c / E^{MSi_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-MoSi$_2$</td>
<td>440 [47]</td>
<td>180</td>
<td>0.41</td>
</tr>
<tr>
<td>Si-WSi$_2$</td>
<td>468 [61]</td>
<td>176</td>
<td>0.38</td>
</tr>
<tr>
<td>Si-VSi$_2$</td>
<td>331 [47]</td>
<td>170</td>
<td>0.51</td>
</tr>
<tr>
<td>Si-NbSi$_2$</td>
<td>363 [61]</td>
<td>172</td>
<td>0.47</td>
</tr>
<tr>
<td>Si-TaSi$_2$</td>
<td>359 [61]</td>
<td>203</td>
<td>0.57</td>
</tr>
<tr>
<td>Si-CrSi$_2$</td>
<td>347 [47]</td>
<td>241</td>
<td>0.69</td>
</tr>
<tr>
<td>Si-TiSi$_2$</td>
<td>265 [47]</td>
<td>211</td>
<td>0.79</td>
</tr>
<tr>
<td>Si-CoSi$_2$</td>
<td>116 [47]</td>
<td>125</td>
<td>1.08</td>
</tr>
</tbody>
</table>

* Composite moduli calculated using $E^c = 150$ GPa

C) Matrix-reinforcement (silicon-disilicide) interfacial strength

Another very important term in Eq. 1.8 is $\gamma^i / \gamma^i$, which in the case of Si-MSi$_2$ alloys, represents the ratio of the fracture energy of the disilicide phase to that of the silicon-disilicide interface. This ratio controls the degree of debonding (Eq. 1.5) which occurs during crack bridging in these materials. Considering the poor low temperature deformability of disilicides (see Section 1.2.2), the contribution to the overall crack opening displacement (Eq. 1.3) from the elastic strain of the disilicides (Eq. 1.4) is expected to be very small. It is therefore essential to maximize $\gamma^i / \gamma^i$ in order to achieve substantial crack opening displacement during crack bridging in these materials. To maximize this ratio, the interfaces should be made weak (i.e. have a low fracture energy) by choosing a Si-MSi$_2$ system that promotes high residual tensile stresses around the disilicide phase. Of course, the interfaces should still have enough strength to enable load transfer to the reinforcing phase. A rough estimation of the magnitude of the residual stresses that arise in the Si-MSi$_2$ alloys (as a result of the thermal expansion and elastic modulus mismatch between the phases) during solidification can be made using the following equations [114] which calculate
the radial/tangential (or circumferential, $\sigma_{rr,\theta\theta}$) and longitudinal ($\sigma_{zz}$) stresses on a fiber when inserted into an infinite matrix of another phase†:

$$\sigma_{rr} = \sigma_{\theta\theta} = \frac{E_f E_m (\alpha_f - \alpha_m)(T_0 - T_A)(1 + \nu_f)}{(1 + \nu_f)E_m (1 - 2\nu_f) + E_f (1 + \nu_m)}$$  \hspace{1cm} (1.11)$$

$$\sigma_{zz} = 2\nu_f \sigma_{rr} + E_f (\alpha_f - \alpha_m)(T_0 - T_A)$$  \hspace{1cm} (1.12)$$

where the subscripts ‘m’ and ‘f’ denote the properties of the matrix and fiber, respectively. For Si-MSi$_2$ alloys, the matrix and fiber properties will correspond with those of silicon and the disilicide phase, respectively. The temperature $T_0$ is that at which the misfit stresses between the fiber and matrix start to arise and $T_A$ is the final temperature. In terms of casting a eutectic alloy, the temperature difference can be assumed to be the cooling range, where $T_0$ is the melting or eutectic temperature of the alloy and $T_A$ is the ambient temperature. The isotropic (i.e. polycrystalline) thermal expansion coefficients for the fiber ($\alpha_f$) and matrix ($\alpha_m$) in the Si-MSi$_2$ eutectic alloys can be estimated by taking the average value of the coefficient from each of the crystallographic directions (Table 1.4) calculated at the respective eutectic temperature (in degrees K) of the alloy (Table 1.5). For example, the coefficients for Si (cubic) and CrSi$_2$ (hexagonal) in Si-CrSi$_2$ would be taken as $\alpha_a / 3$ and $(2\alpha_a + \alpha_e) / 3$, respectively, at $T = 1608.15$ K (1335 °C). Combining these calculations with the elastic moduli values in Table 1.6 and the Poisson’s ratios of the different phases, $\nu_{m,f}$, the residual stresses around the disilicide phase can be determined (results shown Table 1.7).

† The simplified analysis presented here contains some underlying assumptions. First, the temperature at which the matrix-fiber misfit stresses start to arise may be lower than the eutectic temperatures which are used in the calculations of the interfacial stresses. Secondly, the equations used to calculate interfacial stresses assume an infinite matrix, whereas in a real composite, residual stress-field interactions should be taken into account (e.g. by considering the effect of reinforcement volume fraction). Thirdly, this analysis assumes unidirectional, fiber-like reinforcements, which may only be appropriate for certain alloy microstructures. Fourthly, this analysis neglects the presence of any frictional pullout, and thus stresses which may arise due to interfacial roughness or Coulombic interactions between the matrix and reinforcing ligament. Lastly, this analysis does not consider the nature of the chemical bond of the interface, which can have an effect on the interfacial strength.
In all of the Si-MSi\textsubscript{2} eutectic alloys, the reinforcing MSi\textsubscript{2} phases are predicted to be under residual tensile stresses, as should be expected since $\alpha_{\text{MSi}_2} > \alpha_{\text{Si}}$ in every system. This has actually been experimentally observed in Si-VSi\textsubscript{2} eutectic alloys through x-ray studies which showed elastic stretching of the disilicide lattice and elastic compression of the silicon lattice at the interphase boundary [115]. Thus, debonding of the disilicide phase from the silicon matrix should occur in each of the alloys as long as the disilicide does not fail prior to interfacial fracture. Out of all the eutectic systems, the Si-CrSi\textsubscript{2} alloy is estimated to display the highest circumferential and longitudinal tensile stresses around the reinforcing disilicide phase, suggesting an extremely low interfacial fracture energy, and thus extensive debonding, in this composite material. Also of interest is the relatively low tensile longitudinal interfacial stresses in the Si-CoSi\textsubscript{2} alloy which is due to the lower elastic modulus of the CoSi\textsubscript{2} phase. This, in turn, may limit the amount of crack-opening displacement which occurs in this alloy.

In addition to the residual stresses which arise from the differences in thermal expansions of the constituent phases, there are also stresses that can potentially develop from the volumetric changes associated with the liquid-to-solid phase transformation upon solidification. As mentioned in Section 1.3.2, silicon undergoes about a 10 \% volume expansion upon solidification which is in contrast to most metals which shrink as they solidify. The large volumetric differentiation between the nucleating silicon and disilicides phases during eutectic solidification may lead to additional stresses if they are not somehow accommodated by the surrounding environment (e.g. by the liquid phase). At the present moment, however, there is not enough physical understanding of such a phenomenon to accurately provide a quantitative analysis on the solidification expansion/shrinkage effects on residual stresses.
Table 1.7: Estimated circumferential ($\sigma_{rr}, \sigma_{\theta\theta}$) and longitudinal $\sigma_{zz}$ stresses on a MSi$_2$ fiber in an infinite matrix of Si

<table>
<thead>
<tr>
<th>Eutectic Alloy</th>
<th>$\nu_f$</th>
<th>$\sigma_{rr}, \sigma_{\theta\theta}$ (GPa)*</th>
<th>$\sigma_{zz}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-MoSi$_2$</td>
<td>0.150 [47]</td>
<td>1.21</td>
<td>4.63</td>
</tr>
<tr>
<td>Si-WSi$_2$</td>
<td>0.140 [47]</td>
<td>1.08</td>
<td>4.39</td>
</tr>
<tr>
<td>Si-VSi$_2$</td>
<td>0.167 [47]</td>
<td>1.71</td>
<td>5.11</td>
</tr>
<tr>
<td>Si-NbSi$_2$</td>
<td>0.184 [61]</td>
<td>0.98</td>
<td>3.07</td>
</tr>
<tr>
<td>Si-TaSi$_2$</td>
<td>0.189 [61]</td>
<td>1.56</td>
<td>4.83</td>
</tr>
<tr>
<td>Si-CrSi$_2$</td>
<td>0.180 [47]</td>
<td>2.26</td>
<td>6.88</td>
</tr>
<tr>
<td>Si-TiSi$_2$</td>
<td>0.188 [116]</td>
<td>1.94</td>
<td>4.74</td>
</tr>
<tr>
<td>Si-CoSi$_2$</td>
<td>0.335 [117]</td>
<td>1.35</td>
<td>1.41</td>
</tr>
</tbody>
</table>

* Poisson’s ratio of silicon taken to be $\nu_s = 0.225$ [61]

D) Strength of disilicide reinforcements

In addition to the interfacial strength, the other extremely important parameter governing the degree of toughening due to the bridging process is the reinforcement strength. The reinforcement strength contributes to energy dissipated in elastic bridging (Eq. 1.6) by affecting the crack opening displacement (Eqs. 1.3 and 1.4) and the maximum crack closure stress imposed by the reinforcements (Eq 1.7) – the combination of which results in the $(\sigma_f^l)^2$ term in Eq. 1.8. As discussed in Section 1.2.2, disilicides have been reported to display low room temperature fracture strengths. However, these strengths are associated with the bulk form of the material, and are limited by pre-existing defects such as cracks or voids. For the characteristic microstructural size scales commonly associated with rapid eutectic solidification (on the order of $10^0 – 10^2$ μm), the probability of such defects being contained within a single disilicide particle is expected to be small. Within the eutectic alloys, therefore, the disilicide phases should display strengths more representative of their theoretical strengths (i.e. $\sigma_y = H/3$, where H is the hardness), which are extremely high ($\sigma_y \sim 10^3$ MPa) given the high hardness of these materials (H $\sim 10$-20 GPa).
E) Morphology of eutectic microstructure

The last parameter that needs to be taken into account in the design of a eutectic-based reinforced composite is the morphology of the eutectic microstructure. In Section 1.4, the dependencies of the reinforcement shape on crack deflection and bridging were described. Toughening due to crack deflection was shown to be enhanced for reinforcements displaying high aspect ratios (Fig. 1.7). Toughness contributions due to crack bridging were shown to increase with an increasing fiber radius (Eq. 1.8). The geometry of the reinforcing phase is more difficult to directly control for in-situ reinforced composites as compared to those that are artificially reinforced. Fortunately, various theories on eutectic solidification in metallic [118, 119] and ceramic [120] systems have been developed which allow for the prediction and manipulation of the eutectic, and thus reinforcement, morphology.

Eutectic microstructures have been classified into two main categories: normal and anomalous [121]. The different structures which form within these two groups have been summarized [122] in terms of the arrangement and morphology of the major and minor phases. The normal structure can be either lamellar, consisting of regularly spaced plate-like phases within a shared growth direction contained at the interface, or fibrous, which is similar to the lamellar structure but the phases can have a rod-like shape with a polygonal cross-section. In anomalous structures, there is no apparent orientation relationship between the two phases, although the phases generally grow parallel to the growth direction [120]. Anomalous structures have been described as irregular, broken lamellar, fibrous, complex regular, chinese script, and quasi-regular – the definitions of which can be found in [118]. The formation of the different structures has been predicted based on the type of growth (faceted/nonfaceted) of the individual eutectic phases, which has been linked to the roughness of the liquid/solid interface during solidification [123]. In general, it has been found that when the entropy of fusion ($\Delta S_f$) of a phase is low (about less than twice the universal gas constant, $R = 8.314$ J/mol·K), the liquid/solid interface will be atomically rough and nonfaceted growth of the phase will occur due to the ease with which nucleation can occur at the liquid/solid interface. The normal (lamellar and or fibrous) eutectic microstructures tend to form when both phases in a binary eutectic grow in a nonfaceted fashion. On the other hand, if the phase has a very high entropy of fusion, a
smooth liquid/solid interface will result in the faceted growth of the phases with the rate of growth limited by the rate of nucleation at the interface [120]. When one or more phases grow in a faceted manner, one of the anomalous structures tends to form. Both silicon and disilicide phases have entropies of fusion [124] much greater than 2R, and thus are predicted to form a faceted/faceted microstructure composed of independently oriented crystals. However, the actual formation of a faceted/faceted microstructure is quite rare, and it is more likely that the major phase (silicon in most cases) overgrows the faceting minor phase in an unrestricted manner, allowing one of the anomalous structures to form [125].

The type of anomalous eutectic structure that will form for each of Si-MSi₂ systems is dependent on various factors, the most significant of which are perhaps the volume fraction of the second phase and the growth velocity (although surface energies of the crystals and temperature gradients may play a role as well). In many systems, the broken lamellar or fibrous morphologies are stable for minor phase volume fractions below about 0.10 to 0.20, with higher growth rates favoring the fibrous morphology. The instability of the broken lamellar or fibrous morphology leads to the formation of an irregular structure. For minor phase volume fractions around 0.20 – 0.40, the complex regular anomalous structure tends to arise. This complex regular microstructure has many of the features of the normal eutectic microstructure, but instead consists of arrays of short-range regular arrangements of the plate- or rod-shaped phases. However, high growth velocities can cause lower-volume fraction systems to display the complex regular structure [118]. The complex regular structure may also coexist with one or more the other anomalous structures. Beyond a volume fraction of 0.40, the complex regular structure starts to break down which leads to quasi-regular growth during which the minor phase starts locally becoming the matrix phase [122]. This structure consists of arrays of plates or fibers of the non-faceting phase in the “honeycomb-like” matrix of the high entropy phase, and at high growth rates can form a pseudo-colony type structure. Increased growth rates tend to cause the complex regular to quasi-regular morphological transition to occur at lower minor volume fractions [125]. A quasi-regular structure is thought to be desirable for achieving significant

---

‡ A parameter more appropriate than the entropy of fusion, ΔSᵣ, to predict faceted/nonfaceted growth of phases in eutectics containing an intermediate compound is the entropy of solution, ΔSₘ [127]. However, ΔSᵣ was used here due to the availability of thermodynamic data on this parameter for the material systems investigated.
microstructural toughening in in-situ alloys since the locally aligned reinforcing phases within the pseudo-colonies can act as discrete bridging zones. Additionally, this structure forms at large volume fractions of the minor (reinforcing) phase which is in line with the microstructural design criterion to maximize the effectiveness of the crack deflection and bridging mechanisms (Section 1.4.1).

One aspect of the eutectic morphology that has been directly observed to affect the mechanical properties of ceramic-based eutectic in-situ composites is the interlamellar (or interrod) spacing. Many experiments have found the interlamellar spacing to be proportional to the inverse square root of the solidification rate [123, 126-129]. Vickers indentation studies (see [120] and the references therein) have shown that decreases in the interlamellar spacing (due to faster solidification rates) result in improved fracture toughness and hardness of directionally solidified ceramic-based eutectic alloys. Wear resistance was also seen to improve with decreased interlamellar spacing. For anomalous eutectic alloys that exhibit a colony type structure, the fracture toughness has been observed to increase with colony size up to a certain limit where it becomes independent of the colony size and is governed instead by the interlamellar spacing and orientation of the colonies [130].

III) Selection of a silicon-disilicide eutectic system

Comparison of the potential for the different Si-MSi₂ systems to provide for various toughening mechanisms highlights a few favorable systems. Perhaps the most noteworthy advantage is the ability of the Si-TaSi₂, Si-CrSi₂, Si-TiSi₂, and Si-CoSi₂ eutectic systems to produce a volume fraction of the disilicide phase in excess of 0.20, which is the volume fraction generally found to be necessary in achieving substantial toughening through crack deflection and bridging mechanisms (Part II-A). These four systems also display the highest ratios of \( \frac{E^c}{E^{MSi_2}} \), which has been shown to enhance the fracture toughness of composites displaying the crack bridging mechanisms (Part II-B). Both the reinforcement volume fraction and \( \frac{E^c}{E^{MSi_2}} \) ratios increase in the following order: Si-TaSi₂ < Si-CrSi₂ < Si-TiSi₂ < Si-CoSi₂. Estimates of the relative matrix-reinforcement interfacial strengths (Part II-C) based solely on calculations of the residual stresses which arise during processing of the eutectic alloys, reveals that Si-CrSi₂ should contain
the weakest interfaces (i.e. contain highest interfacial residual tensile stresses), whereas Si-CoSi₂ should contain the strongest. The Si-CoSi₂ alloy is a poor candidate in this respect since weak interfaces are desired for debonding of the interfaces during crack deflection, which leads to enhanced crack opening displacements due to bridging. According to theories on eutectic solidification (Part II-E) and observations in actual ceramic-based eutectic systems [131], the eutectic systems which have a tendency to solidify with the desired quasi-regular morphology are those which have $V_f^{MSS} > 0.40$; for the four primary candidate Si-MSi₂ this corresponds to the Si-CrSi₂, Si-TiSi₂, and Si-CoSi₂ systems.

In addition to comparing the predicted toughening attainable using each of the Si-MSi₂ eutectic systems, other factors should be considered when choosing a materials system from which to develop an in-situ toughened engineering composite. To distinguish between the four candidate systems even further, one may first consider the densities of the eutectic alloys based on a rule of mixtures. Taking the volume fractions of the various phases in the alloys (Table 1.5) and their respective densities (Table 1.3), the densities of the four eutectic alloys are found to be 4.08 g/cm³ (Si-TaSi₂), 3.57 g/cm³ (Si-CrSi₂), 3.42 g/cm³ (Si-TiSi₂), and 4.27 g/cm³ (Si-CoSi₂). In terms of density, the Si-CrSi₂ and Si-TiSi₂ alloys are most likely to be competitive with powder processed engineering ceramics which tend to have densities less than 4 g/cm³. Due to the potential toughening in these alloys, they may also be competitive in terms of their specific mechanical properties, such as specific strength and specific toughness (Fig 1.1.). However, perhaps an even clearer discernment between the potential eutectic alloys to be used as viable commercial engineering materials can be made by comparing the prices of the alloying elements. Although exact market prices of the alloying elements are difficult to define due to their constant fluctuations, a comparison of the prices of the elements from different suppliers show that Cr and Co are similar in cost and are about three to four times cheaper than Ti and over ten times cheaper than Ta. In terms of material costs, the Si-CrSi₂ eutectic system has the advantage over Si-CoSi₂ eutectic system in that it requires less of the alloying element: 21.7 wt.% Cr vs. 37.9 wt.% Co (Table 1.5). The relatively low material cost of the Si-CrSi₂ eutectic makes it a very attractive material system to use in developing a silicon-based composite alloy, which already has the cost benefit of using (low purity) silicon as the primary constituent.
In addition to the physical, mechanical, and economic benefits of the Si-CrSi$_2$ eutectic system, one final advantage of this system is the large alloying opportunities available to create silicon-disilicide composites based on higher order material systems. As mentioned in Section 1.3.1, the C40 disilicides have larger solubilities for other alloying elements compared to the other disilicide structures – for instance, the C54 (TiSi$_2$) and C1 (CoSi$_2$) structures. In fact, all of the C40-type disilicides are completely soluble in one another (Fig. 1.6). This opens up the possibility of alloying Si-CrSi$_2$ with additional transition metals to enable a more variable control over the silicon-disilicide composite microstructure to compensate for any shortcomings of the binary eutectic system. A review of the other transition metals shows that vanadium is a potentially useful ternary alloying addition in the Si-CrSi$_2$ binary system. First, VSi$_2$ is completely soluble in CrSi$_2$ (as both are C40 structures), and thus V can be substituted for Cr over the entire composition range to create a Si-(Cr,V)Si$_2$ alloy without any changes in the crystal structure of the second phase. This can have major implications in the resulting form of the ternary phase diagram which will be needed to predict the solidification paths of alloys in this system (this is discussed in Chapter 2). Second, VSi$_2$ has the second lowest density next to TiSi$_2$ (Table 1.3) which means vanadium substitutions can be used to decrease the density of the overall Si-(Cr,V)Si$_2$ composite compared to the binary Si-CrSi$_2$ alloy. Of course, large amounts of V substitutions come at a cost since the price of V is about 4-5 times that of Cr. Finally, the Si-VSi$_2$ system produces a very different volume fraction of disilicide phase compared to the Si-CrSi$_2$ system ($V_f^{VSi_2} = 0.112$ versus $V_f^{CrSi_2} = 0.461$) as shown in Table 1.5. This, in addition to the complete solubility of the two phases, suggests that the volume fraction of the reinforcing (Cr,V)Si$_2$ phase can be easily controlled by altering the ratio of Cr:V additions in the Si-(Cr,V)Si$_2$ alloy. This is of scientific interest since such a system may allow a systematic investigation of the effects of the disilicide volume fraction on the resulting microstructural and fracture properties of Si-MSi$_2$ composites – this is the focus of Chapter 3.

1.5 Problem statement and research objectives

As the title suggests, the purpose of this chapter was to describe, in detail, how an in-situ toughened alloy or composite can be designed on the basis of various properties of the overall material system, as well as those of the individual constituent phases, from which the alloy is
composed. This is an extremely useful exercise because it allows for the a priori selection of a few optimal material systems to be thoroughly studied without the need to narrow down the selection through an experimental survey of many different material systems – a task which can be both costly and time consuming. In the case of the development of a castable in-situ toughened silicon-rich alloy, different types of Si-X systems were reviewed with a major emphasis on systems in which X is a transition metal disilicide (MSi$_2$). Based on the discussions in Sections 1.1-1.4, the ternary Si-Cr-V system was chosen as the material system from which to develop Si-(Cr,V)Si$_2$ composites. The subsequent three chapters of this thesis, which are briefly described below, are divided into the major research tasks of this thesis:

- Due to the lack of interest in silicon-rich alloys as structural materials, many of the details of the phase diagrams of high order Si-based material systems are currently unknown. Of particular importance is the location of the eutectic boundary curves (similar to the eutectic points in binary systems, see Part I of Section 1.4.2), since the minimization or elimination of primary silicon/disilicide solidification in cast alloys requires that the nominal composition lay near or on those curves. For this work, the phase diagram of interest is the Si-rich portion of the Si-Cr-V system (i.e. the Si-CrSi$_2$-VSi$_2$ system). In Chapter 2, the Si-CrSi$_2$-VSi$_2$ phase diagram will be derived using a coupled experimental-computational approach, known as CALPHAD [132]. In this approach, all theoretical and experimental phase diagram, thermodynamic, and structural data which has been gathered for the constituent binary systems within the ternary Si-Cr-V system, can be used to develop a multi-component database from which Gibbs energy functions can be modeled for phases for which such functions are currently undefined. Comparison of these models with actual experimental data (e.g. calorimetry, microstructural analysis) allows for the optimization of the Gibbs energy functions, and thus an accurate thermodynamic description of the phase diagram.

- An application of composite design theory to the development of in-situ toughened silicon-disilicide eutectic alloys (Section 1.4) suggested that these
materials should display toughening mechanisms such as crack deflection and bridging, and that such toughening mechanisms should lead to a rising R-curve behavior where the apparent fracture toughness increases with crack extension (Fig 1.9). Up until now, such fracture behavior has not been observed, and thus characterized, for these types of materials due to either the small size scale at which these materials have been fabricated (i.e. thin films, coatings, etc.) or the inability of previous mechanical tests to measure long-crack behavior of the alloys (as in the Vickers indentation tests used in Forwald’s [5] work). In Chapter 3, the long-crack behavior of Si-(Cr,V)Si₂ alloys will be studied using chevron-notched beam (CNB) tests. The influence of microstructural features such as the volume fraction of the disilicide phase, interlamellar or interrod spacing, and the presence of primary phases on microstructural toughening will be assessed. In addition, in-situ CNB testing will be performed to observe crack-microstructure interactions during crack growth so that a fundamental understanding of the fracture behavior of Si-(Cr,V)Si₂, as well as other Si-MSi₂, alloys, may be gained.

- Many engineering ceramics are used as structural materials due to their excellent triobological properties (i.e. wear resistance). The wear resistance of brittle materials, such as ceramics, is highly dependent on their hardness and fracture toughness. Silicon’s hardness (H ≈ 8 – 14 GPa [133]) is in the same range as those displayed by engineering ceramics, yet its wear resistance is very poor [134] due to its extremely low fracture toughness. However, the potential for improved fracture resistance of in-situ toughened Si-MSi₂ alloys may allow these materials to be used as tribological components in applications currently dominated by conventional powder processed ceramics. In Chapter 4, ball-on-disk tests will be used to measure the wear resistance of several Si-(Cr,V)Si₂ alloys. The resulting wear behaviors will be analyzed in terms of the microstructural features which govern the fracture, and hence, wear properties of these materials (i.e. those analyzed in Chapter 3). By performing ball-on-disk tests at various loads, the wear properties of the Si-(Cr,V)Si₂ alloys may be analyzed in both the mild and severe wear regimes. The experimental data is compared with predictions based
on a wear model which considers the contribution of fracture toughness to the wear resistance of a given material. This type of comparison sheds light on the effects of R-curve behavior on the tribological properties of in-situ toughened silicon-rich alloys.
Chapter 2: Thermodynamic assessment of the Si-rich corner of the Si-Cr-V phase diagram: the Si-CrSi$_2$-VSi$_2$ system

2.1 Necessity of Si-CrSi$_2$-VSi$_2$ phase diagram for processing of in-situ toughened Si-(Cr,V)Si$_2$ alloys

As the development of in-situ toughened Si-rich alloys is a relatively untapped area of research, it is no surprise that there is very little data available on the phase diagrams for ternary and higher order Si-rich systems – including that of Si-CrSi$_2$-VSi$_2$, from which the present Si-(Cr,V)Si$_2$ alloys are based. Knowledge of diagram features such as ternary eutectic points or eutectic boundary curves are necessary in optimizing the alloy microstructures by being able to predict and control the degree of primary solidification that occurs during processing. This is of particular importance for silicon-disilicide alloys, where formation of primary Si grains during anomalous eutectic solidification (Section 1.4.2 Part II-E) can lead to excessive overgrowth of the silicon phase, and thus degradation of the alloy’s fracture properties (more about this topic will be discussed in Chapter 3). In this chapter, a combined experimental-computational approach is taken for the determination of the Si-CrSi$_2$-VSi$_2$ system. Once attaining an accurate thermodynamic description (i.e. free energy functions) of the phases present in the system, equilibrium solidification paths are simulated for specific alloy compositions studied in both the fracture (Chapter 3) and wear (Chapter 4) experiments. In those experiments, a comparison is made between the phase fractions predicted from the present equilibrium thermodynamic calculations and those actually observed from non-equilibrium processing conditions. This will help to elucidate the significance of non-equilibrium effects, such as solute segregation, on the resulting microstructures of cast Si-(Cr,V)Si$_2$ alloys.

2.2 Experimental Procedures

2.2.1 Differential scanning calorimetry and microstructural analysis

Differential scanning calorimetry (DSC) experiments were carried out using a Mettler-Toledo TGA/DSC 1 STAR® system with a high temperature furnace. Prior to experimentation, heat flow
and temperature calibrations of the system were performed using certified reference standards of In, Zn, In, Au, and Pd. The starting materials for the Si-(Cr,V)Si₂ alloys [granular silicon (99.999 %), chromium powder (99.996 %), and vanadium granules (99.7 %)] were all measured out to within 0.1 wt. % of the desired compositions using a Sartorius ME36S microbalance with a resolution of +/- 2 μg. The total mass of the alloys ranged between 40 and 50 mg, which was found to allow for complete homogenization of the alloys during the melting procedure while providing a large contact area with the base of the sample pan. The raw materials were placed in 70 μL Al₂O₃ pans inside of the furnace chamber on a DSC thermal sensor alongside a blank Al₂O₃ reference pan of the same volume. Before running each experiment, the furnace chamber was allowed to become filled with Ar at 25 °C for 1 hr, after which each experiment was run under the flowing Ar. An experimental method was created which allowed the alloys to be both processed and analyzed during a single thermal cycle. First, the raw materials were heated to a temperature of 1600 °C where they were melted and held for 30 min as to allow complete mixing to occur. The liquid alloy was then rapidly cooled (~100 °C/min) to 1100 °C and isothermally held for 30 min, after which it was heated back up to 1550 °C at a rate of 5 °C/min. During the final ramp-up stage, both the heat flow (± 0.1 mW) and mass ( +/- 1 μg) of the sample was recorded (additional details of the DSC experimental design are presented in appendix A). Phase transition temperatures and enthalpies of melting (ΔHm) were measured from the resulting endothermic peaks. A tangential baseline was employed for the peak integrations used in the enthalpy determinations. The liquidus temperatures (Tm) were taken as the peak temperatures of the endothermic peak (or of the last endothermic peak for alloys displaying multiple thermal signals).

In addition to thermal analysis of binary and ternary Si-(Cr,V)Si₂ alloys, the melting behavior of the reinforcing (Cr,V)Si₂ disilicide phase (i.e. compositions along the CrSi₂-VSi₂ binary join) was also studied. For these materials, pure CrSi₂ (99+ %) and VSi₂ (99.5 %) powders were pressed into pellets (30 – 50 mg) which were then arc melted in an MRF (Materials Research Furnace) ARC/SA-200 furnace which was evacuated down to between 10⁻² – 10⁻³ torr and back-filled with Ar. The arc was created between a tungsten electrode and a water-cooled copper hearth (in which the pellet was contained) using a current of 200 A. Three melts were performed for each specimen as to ensure complete homogenization of the sample. The DSC method used
for these samples consisted of remelting the specimens at 1600 °C for 5 min, rapidly quenching the melt (~100 °C/min) to 1100 °C and isothermally holding for 30 min, and finally heating to 1600 °C at 5 °C/min during which thermal data was collected and analyzed in a manner similar to that previously described for the Si-(Cr,V)Si₂ alloys.

The approach taken to experimentally map out the phase diagram using the experimental methodology described above is schematically depicted in Fig 2.1. First, the eutectic points for the Si-VSi₂ (e₁) and Si-CrSi₂ (e₂) binary systems were identified. These values were compared to those cited in the literature for the binary systems as a check of the reliability of the experimental procedure used in this study. Eutectic compositions were identified within the ternary phase field by analyzing the thermal behavior of alloy compositions along isoplethic sections of constant Si composition that traversed the region between the two binary eutectic compositions (denoted by dotted lines). The potential eutectic compositions were identified as those alloys that displayed only a single melting peak (as opposed to those displaying multiple peaks and hence the presence of a primary phase). For alloys where the eutectic and primary melting peaks could not be resolved, microstructural analysis of the DSC specimens was used to select the appropriate eutectic composition for the given isoplethic section.

2.2.2 Computational thermodynamics – the CALPHAD approach

Computational thermodynamic calculations were carried out using Thermo-Calc® software to determine the Si-CrSi₂-VSi₂ phase diagram for comparison against the experimental measurements. These calculations are based on the CALPHAD method of determining equilibrium states through the global minimization of the total free energy of the material system. The method considers the molar Gibbs free energy of all phases (θ) which are generally described by the following expression:

\[
G_m^{\theta} = G_m^{\theta} - \sum_i b_i H_i^{SER} = G_m^{\theta} + G_m^{\theta} - T^{\text{conf}} S_m^{\theta} + E_m^{\theta}
\]  

(2.1)
Figure 2.1: Schematic of the DSC experimental approach used to identify the eutectic alloy compositions within the Si-CrSi$_2$-VS$_2$ ternary phase field. First, the Si-VS$_2$ (e$_1$) and Si-CrSi$_2$ (e$_2$) binary eutectic compositions were identified. Afterwards, alloy compositions along Si isopleths which traversed the two binary eutectic points were studied. Eutectic compositions were identified by those that displayed a single melting peak and contained a eutectic microstructure (as determined by microstructural analysis of the tested DSC specimen).

where $^{srf}G_m^\theta$ (known as the surface of reference) is the Gibbs energy of an unreacted mixture of the constituents of the phase, $^{phys}G_m^\theta$ represents the Gibbs energy due to a physical model (such as magnetic transitions), $^{cnf}S_m^\theta$ is the configurational entropy of the phase, and $^EG_m^\theta$ is the excess Gibbs energy [135]. The term $G_m^\theta - \sum_i b_i H_i^{SER}$ is shown here to clarify that the Gibbs energy for all phases are taken with respect to the same reference point for each element, where $H_i^{SER}$ is the molar enthalpy of the elements in their standard element reference states at 298.15 K and 1 bar and $b_i$ is the stoichiometric factor of element $i$ in the phase $\theta$. This term is needed because there is no absolute value for the Gibbs energy [135]. Various models for $G_m^\theta$ have been developed for different types of phases. In the present work, the term $^{phys}G_m^\theta = 0$ for all the phases considered.
For the stoichiometric phases (ex. $\alpha$Cr$_5$Si$_3$, CrSi, V$_5$Si$_3$, and V$_6$Si$_5$), the various contributions to the total Gibbs free energy (Eq. 2.1) are given by the following equations:

\begin{align}
^{\text{sf}} G_m^\theta &= x_A^0 G_A^0 (T) + x_B^0 G_B^0 (T) \\
^E G_m^\theta &= \Delta G_{^A_A^B}^{^A_B^B} (T)
\end{align}

where $x_A$ and $x_B$ are the mole fractions of elements A and B given by the stoichiometry of the compound; $^0 G_A (T)$ and $^0 G_B (T)$ are the Gibbs free energies of elements A and B with respect to their reference states (i.e. bcc for Cr and V and diamond for Si); and $\Delta G_{^A_A^B}^{^A_B^B} (T)$ is the Gibbs energy of formation of the compound referred to the stable elements at temperature $T$ [136].

The contributions to the Gibbs free energy for the solution phases (ex. liquid) are described by a substitutional regular-solution model:

\begin{align}
^{\text{sf}} G_m^\theta &= \sum_{i=1}^{n} x_i^0 G_i^\theta (T) \\
^{\text{cnf}} S_m^\theta &= -R \sum_{i=1}^{n} x_i \ln(x_i) \\
^E G_m^\theta &= \sum_{i \neq j} x_i x_j L_{ij} (T)
\end{align}

where $x_i$ refers to the mole fractions of the pure element $i$, $G_i^\theta (T)$ is the Gibbs free energy of the element $i$ in the solution phase, and $R$ is the universal gas constant ($= 8.314 \text{ J/mol} \cdot \text{K}$). The excess Gibbs free energy term (Eq. 2.3c) is the Redlich-Kister (RK) [137] polynomial expression, where the composition dependence of the interaction parameters, $L_{ij} (T)$, between elements $i$ and $j$ is given by:
\[ L_{ij}(T) = \sum_{v=0}^{k} \left( x_i - x_j \right)^v L_{ij}(T) \]  

(2.4)

When the RK coefficient \( v = 0 \), this expression is simply called a regular solution model. The expression is called a subregular-solution model when two RK coefficients are employed (\( v = 0 \) and 1). Ternary and higher order excess Gibbs energy contributions were not considered in this study.

A two-sublattice model [138, 139] was used to describe the ordered phases (bcc-A2, Cr3Si, \( \beta \)Cr5Si3, CrSi2, and V3Si) where the respective surface of reference and configurational entropy terms are given by:

\[
\begin{align*}
\text{surf } G_m^o &= \sum_i \sum_j y'_i y''_j G_{ij}(T) \\
\text{conf } S_m^o &= -R \left( m \sum_i y'_i \ln(y'_i) + n \sum_j y''_j \ln(y''_j) \right)
\end{align*}
\]  

(2.5a)  

(2.5b)

The colon in the subscript of the \( G_{ij}(T) \) term is used to identify the separate constituents on each of the sublattices. When the elements \( i \) and \( j \) are the same, \( G_{ij}(T) \) represents the Gibbs energy of formation of the constituent elements; when they are different, it represents the Gibbs energy of formation of the compound \( A_mB_n \) or \( B_mA_n \) (where A and B are the elements \( i \) and \( j \)). The terms \( y'_i \) and \( y''_j \) are the constituent fractions on sublattices 1 and 2, respectively, and the factors \( m \) and \( n \) give the ratio of the sites on the two sublattices. For an ordered phase consisting of only two constituents which can exist on either sublattice (i.e. \( (A,B)_m(A,B)_n \)) , the excess free energy term is equal to:

\[
\begin{align*}
\text{conf } G_m^O &= y'_A y''_B [y''_A L_{A,B:A}(T) + y''_B L_{A,B:B}(T)] + y'_A y''_B [y'_A L_{A:A,B}(T) + y''_B L_{B:A,B}(T)] \\
&+ y'_A y''_B y'_A y''_B L_{A,B:A,B}(T)
\end{align*}
\]  

(2.5c)
The interaction parameters in the above equation are expressed by the same RK polynomial as in Eq. 2.4. It is assumed that the interaction on each sublattice is independent of the occupation of the other sublattice such that:

\[ L_{A,B,*}(T) = \sum_{v=0}^{n} (y_A^v - y_B^v)^v \cdot L_{A,B,*}(T) \]  

(2.6)

where * can be any constituent. Similar expressions for the excess free energy term in Eq. 2.5c can be derived for cases where additional constituents exist on one or both of the sublattices, just as long as all possible interactions are taken into account. Site defects such as vacancies can also be considered as a constituent in addition to the elements.

The temperature dependence of the \( G(T) \) terms on the right-hand side of Eqs. 2.2a,b, 2.3a, and 2.5a are all usually described by the same power series in temperature such that the overall temperature dependence of \( G_m^\theta \) is:

\[ G_m^\theta - \sum_i b_i H_i^{SER} = a_0 + a_1 T + a_2 T \ln(T) + a_3 T^2 + a_4 T^{-1} + \cdots, T_1 < T < T_2 \]  

(2.7)

Normally only the first two coefficients, \( a_0 \) and \( a_1 \), are adjusted during optimization of the phase descriptions unless the heat capacity (\( C_p \)) is known as a function of the temperature since \( C_p \) is related to the coefficients \( a_2, a_3, a_4 \) etc. by the relation:

\[ C_p = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_{P,N_i} \]  

(2.8)

The temperature dependence of the interaction parameters in Eqs. 2.4 and 2.6 which are used to calculate the excess free energy terms for the phases can have the same temperature dependence as given in Eq. 2.7 for the Gibbs energy terms. However, a linear temperature dependence is conventionally used (Eq. 2.9) and only when heat capacity data is known are the higher order
terms employed. The coefficients $\gamma a_{ij}$ and $\gamma b_{ij}$ are both adjustable parameters that are optimized during assessment of the thermodynamic description of a materials system.

$$\gamma L_{ij} = \gamma a_{ij} + \gamma b_{ij} T$$  \hspace{1cm} (2.9)

The extrapolation of binary excess parameters (Eqs. 2.3c and 2.5c) to the ternary phase field was performed using the Muggianu method [140]:

$$\phi G_m^e = x_A x_B \left[ L_{AB}^0 + L_{AB}^1 (x_A - x_B) \right] + x_B x_C \left[ L_{BC}^0 + L_{BC}^1 (x_B - x_C) \right] + x_A x_C \left[ L_{AC}^0 + L_{AC}^1 (x_A - x_C) \right]$$  \hspace{1cm} (2.10)

All of the thermodynamic parameters used for the present phase diagram calculations are listed in Table B.1 of the appendix. The Gibbs free energy models used in the present study are based on the current optimizations of the Si-V system by Zhang et al. [141] and of the Si-Cr system by Du et al. [142], with the modification of (Cr,V)Si$_2$ modeled as a single phase. The Gibbs energies for the pure elements are taken from the Scientific Group Thermodata Europe (SGTE) compilation by Dinsdale [143].

### 2.3 Experimental Results

#### 2.3.1 Experimental determination of Si-CrSi$_2$-VSi$_2$ system

1) Binary Si-CrSi$_2$ and Si-VSi$_2$ systems

A set of DSC curves measured for alloy compositions along the binary Si-CrSi$_2$ line are shown in Fig. 2.2 (all compositions are given in at. %). For alloys Si-4.00Cr and Si-6.04Cr, two endothermic peaks are present in the DSC signal, clearly indicating the presence of primary silicon. As the alloy composition becomes enriched in Cr, the primary peak approaches and eventually becomes subsumed by the eutectic peak. Further additions of Cr to the alloy cause the single-peak to revert back to the double-peak shape since complete melting of the alloy
occurs at a higher temperature. In this case, the primary peak refers to the CrSi$_2$ phase instead of Si. Possible eutectic compositions were thus identified by those displaying a single peak in their thermal signal. A similar analysis was performed for binary Si-V alloys to identify possible eutectic compositions along the Si-VSi$_2$ line. Final determination of the binary eutectic points was made through microstructural analysis of the candidate alloys selected from the DSC experiments. The binary Si-VSi$_2$ and Si-CrSi$_2$ eutectic compositions ($C_e$) and reaction temperatures ($T_e$) were found to be Si-3.99V ($T_e = 1386 \, ^\circ C$) and Si-12.09Cr ($T_e = 1338 \, ^\circ C$), respectively. These values are in good agreement with those reported in the ASM binary phase diagram handbook [113] for the Si-VSi$_2$ ($C_e = Si-3V$, $T_e = 1400 \, ^\circ C$) and Si-CrSi$_2$ ($C_e = Si-13Cr$, $T_e = 1328 \, ^\circ C$) eutectic reactions. Micrographs for both alloys (Fig. 2.3) revealed (near) fully eutectic microstructures, with no primary or overgrown silicon or disilicide phase regions. The binary Si-VSi$_2$ eutectic alloy (Fig 2.3a) displayed a fibrous eutectic structure, while that of the binary Si-CrSi$_2$ eutectic alloys (Fig. 2.3b) displayed a colony type structure. A more descriptive analysis of the anomalous eutectic structures of Si-(Cr,V)Si$_2$ alloys is presented in Chapter 3 (Section 3.3.1). Thermodynamic data, including the liquidus temperatures and enthalpies of melting, for all of the alloys investigated within the Si-CrSi$_2$ and Si-VSi$_2$ binary systems are given in Tables B.2 and B.3 (respectively) of the appendix.
Figure 2.2: A set of DSC curves for alloy compositions along the binary Si-CrSi₂ line reveals a change in the number of endothermic peaks measured as the alloy passes through the eutectic composition. Alloys containing a relatively high degree of primary Si (Si-4.00Cr, Si-6.04Cr) or CrSi₂ (Si-20.20Cr) have a distinguishable second peak. Such DSC data was used to select possible eutectic compositions (i.e. single-peaked curves) for further microstructural analysis and final identification of the eutectic alloy (Si-12.09Cr in this case). A similar analysis was performed for the Si-VSi₂ binary system. (All compositions are given in at. %).
Figure 2.3: Micrographs of the binary (a) Si-3.99V and (b) Si-12.09Cr alloys that were selected as the Si-VSi₂ and Si-CrSi₂ eutectic compositions, respectively. Both alloys displayed (near) fully-eutectic structures containing no primary or overgrown silicon or disilicide phase regions. The eutectic structures were (a) fibrous and (b) colony type. In these micrographs, the darker regions are the Si phase and the brighter regions are the respective VSi₂ and CrSi₂ phases.

II) Binary CrSi₂-VSi₂ system: the (Cr,V)Si₂ phase

Three DSC curves for alloy compositions along the CrSi₂-VSi₂ binary line are shown in Fig. 2.4. The top curve corresponds to the binary CrSi₂ phase (Cr₃₃.₃Si₆₆.₇), whereas the second and third curves correspond to mixed (Cr,V)Si₂ compounds that were made using disilicide powder ratios of 90 % CrSi₂ - 10 % VSi₂ [(Cr₂₉.₉₇,V₃.₃₃)Si₂] and 80 % CrSi₂ - 20 % VSi₂ [(Cr₂₆.₆₄,V₆.₆₆)Si₂], respectively. Multiple endothermic peaks present in the curves indicate that obtainment of a single disilicide phase was not achieved in the specimens prior to thermal analysis. Although the specimens contained secondary phases, analysis was still performed on the main disilicide melting peaks to assess the behavior of the liquidus temperature with variation of the compound’s Cr:V ratio. The liquidus temperature measured from the binary CrSi₂ peak was found to be 1439 °C (ΔHₘ = 48.5 kJ/mol) which agrees with the melting temperature given for CrSi₂ in the ASM binary phase diagram handbook [113] (Tₘ = 1439 °C) and is close to the enthalpy of melting given by Chart [144] (ΔHₘ = 42.6 ± 1.5 kJ/mol). Liquidus temperatures measured from the (Cr₂₉.₉₇,V₃.₃₃)Si₂ and (Cr₂₆.₆₄,V₆.₆₆)Si₂ disilicide peaks were found to be 1455 °C and 1499 °C, respectively. Broadening of the main disilicide peak in these two alloys with increasing V content, however, suggests an increase in the variation of the specimen composition.
(i.e. decrease in the homogeneity) and hence reduced reliability of the absolute liquidus measurements. Nonetheless, a clear shift of the main peak in the DSC signals to higher temperatures implies a monotonic increase in the melting temperature of (Cr,V)Si₂ with increasing V content. Therefore, no binary minimum point is expected to exist along the CrSi₂-VSi₂ binary line.

Figure 2.4: DSC curves for alloy compositions along the CrSi₂-VSi₂ binary line show a clear shift in the disilicide peak position to higher temperatures as the V content is increased. This suggests that the melting point of the (Cr,V)Si₂ phase monotonically increases along the binary line from CrSi₂ to VSi₂. However, the multiple peaks in the DSC signals indicates that these disilicide compounds are not free of secondary phases and thus caution should be made in acceptance of the absolute melting temperatures as measured from these peaks – especially at higher V contents where peak broadening is observed to occur due to large variations in the alloy compositions.
III) Ternary Si-CrSi₂-VSi₂ system

Calorimetric and microstructural analysis of six isoplethic sections of constant Si (Fig. 2.5) was performed in order to map the eutectic boundary curve between the binary Si-VSi₂ (e₁) and Si-CrSi₂ (e₂) points found in Part I. Alloy compositions along each isopleth in Fig. 2.5 are labeled alphabetically starting from left to right. Throughout the chapter, some of the alloys will be referred to by their alphanumeric designation (i.e. alloy 1-a is the composition referring to point ‘a’ on isopleth 1). The thermal data measured for these alloys are listed in Tables B.4 – B.9 of the appendix.

Figure 2.5: Diagram showing the alloy compositions along six isoplethic sections that were experimentally investigated (by combined DSC and microstructural analysis) to determine the eutectic boundary curve between the binary Si-VSi₂ (e₁) and Si-CrSi₂ (e₂) eutectic points found in Part I of this section.
A typical set of DSC curves measured for alloys within the Si-CrSi$_2$-VSi$_2$ ternary phase field are shown in Fig. 2.6 for the series of compositions along isopleth 6 (88.85 at. % Si). Similar to the curves measured for the binary alloys (Fig. 2.2), a clear eutectic endothermic peak is observed for each alloy composition (marked by an asterisk). In this case, the eutectic reaction occurs along a boundary line instead of at a point. Compared to the binary alloys, however, the primary signals are much less resolved. Only through close inspection of the curves (Fig. 2.7) can one identify the points at which eutectic melting ends (i.e. the composition leaves the eutectic boundary curve) and the primary melting begins. This is due to the fact that the composition of the (Cr,V)Si$_2$ disilicide phase is variable (i.e. $x$(Cr) + $x$(V) = 33.3 at. %) in the ternary phase field, as opposed to being constant (i.e $x$(Cr) or $x$(V) = 33.3 at. %) for the binary systems. The variability of the disilicide composition upon solidification/melting (which is governed by the relevant tie lines of the ternary phase diagram) has an analogous effect on the DSC thermal signals as shown in Fig. 2.4. That is, wide distributions of the (Cr,V)Si$_2$ composition cause the endothermic peaks to become broader and flatter compared to the binary compound.

**Figure 2.6:** DSC curves for alloy compositions along the 88.85 at. % Si isopleth (isopleth 6 in Fig. 2.5) display sharp eutectic peaks corresponding to melting along the eutectic boundary curve. The primary peaks for alloy compositions in the ternary phase field are less distinct than for binary compositions (Fig. 2.4) due to the variability of the (Cr,V)Si$_2$ composition (i.e. changes in the Cr:V ratio) as opposed to the constant binary CrSi$_2$ or VSi$_2$ compositions demanded by stoichiometry.
Figure 2.7: Magnified view of the primary (Cr,V)Si$_2$ peaks identified in Fig. 2.6. As the degree of primary (Cr,V)Si$_2$ solidification is increased [from alloy (f)-(a)], the primary peaks become more removed from the initial eutectic peak since the liquidus temperature of the alloy increases.
After having identified possible eutectic compositions for each of the six isopleths (in the same manner as described above for isopleth 6), complimentary microstructural analysis of the selected alloys was performed in order to determine the compositions corresponding to the points along the eutectic boundary curve. An example of this is shown for alloys 3b-3d (92.62 at. % Si isopleth) in Fig. 2.8. Alloy 3b (Fig. 2.8a) contained large disilicide grains identified as primary (Cr,V)Si₂. As the alloy composition traversed along the isopleth towards the Si-CrSi₂ binary line (i.e. from 3b-3d), the microstructure changed to a near fully-eutectic microstructure composed of eutectic colonies (Fig. 2.8b), to one composed of large primary Si grains (Fig. 2.8c). Thus, alloy 3c was concluded to be the alloy composition lying closest to the eutectic boundary curve separating the regions of primary (Cr,V)Si₂ and Si solidification. The microstructures of all the alloys identified as lying along the eutectic boundary curve for each isoplethic section are shown in Fig. 2.9.

![Figure 2.8](image)

**Figure 2.8:** Series of micrographs for alloy compositions 3b – 3d (92.62 at. % Si isopleth) showing a transition from (a) primary (Cr,V)Si₂ solidification to (b) eutectic solidification to (c) primary Si solidification as the compositions traverses the ternary eutectic curve.
Figure 2.9: Micrographs of the alloy compositions that were experimentally determined to lie along the eutectic boundary curve within the Si-CrSi$_2$-VSi$_2$ ternary system. A eutectic point was identified for each of the 6 isopleths in Fig. 2.5.
2.3.2 Computational determination of Si-CrSi$_2$-VSi$_2$ system

I) Binary Si-CrSi$_2$ and Si-VSi$_2$ systems

Figure 2.10 shows the respective binary Si-CrSi$_2$ and Si-VSi$_2$ phase diagrams calculated using the thermodynamic database (Table B.1 of the appendix) based on the current optimizations of the Si-V system by Zhang et al. [141] and of the Si-Cr system by Du et al. [142]. Both diagrams are very consistent with those most commonly reported in widely accepted phase diagram references such as [113, 136]. Table 2.1 lists the relevant data for the reactions between the disilicide and silicon end members of each system (the values in parenthesis are from the experimental determinations of the binary eutectic reactions discussed in Section 2.3.1 Part I). Experimental and calculated eutectic compositions were found to differ only by 2.5 at. % Si for the Si-CrSi$_2$ reaction and by 0.9 at. % Si for the Si-VSi$_2$ reaction. Additionally, the melting points of Si, CrSi$_2$, and VSi$_2$ are all in very good agreement with presently reported values [111] for these phases ($T_m$(Si) = 1414 °C, $T_m$(CrSi$_2$) = 1439 °C, $T_m$(VSi$_2$) = 1677 °C). Based on this assessment, the thermodynamic descriptions for the binary Si-CrSi$_2$ and Si-VSi$_2$ systems were deemed acceptable.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Composition (at.% Si)*</th>
<th>Temp (°C)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>L → Si</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>L → CrSi$_2$</td>
<td>- 66.6</td>
<td>-</td>
</tr>
<tr>
<td>L → CrSi$_2$ + Si</td>
<td>85.4 (87.9) 66.6 100</td>
<td>1328 (1338)</td>
</tr>
<tr>
<td>L → VSi$_2$</td>
<td>- 66.6</td>
<td>-</td>
</tr>
<tr>
<td>L → VSi$_2$ + Si</td>
<td>95.1 (96.0) 66.6 100</td>
<td></td>
</tr>
</tbody>
</table>

* Values in parenthesis correspond to experimental values from Section 2.3.1
Figure 2.10: Calculated binary phase diagrams for the (a) Si-Cr and (b) Si-V systems based on the optimizations in [144] and [143], respectively. The computed eutectic and melting reactions in the Si-MSi$_2$ region of both diagrams agree closely with those experimentally determined in Section 2.3.1 Part I.

As a check on the sensitivity of the calculated thermodynamic quantities on the parameters used to describe the Si-Cr-V system, the two-sublattice model used to describe the CrSi$_2$ phase [(Cr, Si, V)$_1$(Cr, Si)$_2$] (partially reproduced from Table B.1 below) was adjusted so that the calculated Si-CrSi$_2$ eutectic temperature matched the experimental determination listed in Table 2.1. Specifically, the $a_1$ parameter (see Eq. 2.7) in the CrSi$_2$ Gibbs energy of formation term ($a_1 = 336.777$) was adjusted, where $a_1$ is related to $\Delta S$ via the relation $\Delta G = \Delta H - T \cdot \Delta S$. The higher order terms related to heat capacity of the phase (not shown here) were not adjusted. By decreasing $a_1$ from 336.777 to 334.300, the calculated Si-CrSi$_2$ eutectic composition and temperature become Si-12.10Cr (at. %) and 1343 °C, respectively, and agree well with the measure values ($C_e = $ Si-12.09Cr (at. %), $T_e = 1338$ °C). However, due to the increased stability of the CrSi$_2$ phase, the melting temperature of CrSi$_2$ increases to 1496 °C, which is well above that measured for this phase ($T_m = 1439$ °C). Since the melting temperature of the CrSi$_2$ phase is a much more reliable thermodynamic measurement than the eutectic composition and temperature, adjustment of the thermodynamic parameters was considered inappropriate.

\[ \theta G_{CrSi}^{CrSi_2} - H_{Cr}^{SER} - 2H_{Si}^{SER} = -100,352.65 + 336.777 \cdot T + \cdots \]  
(from Table B.1)
II) Binary CrSi$_2$-VSi$_2$ system: the (Cr,V)Si$_2$ phase

The liquidus temperature of the (Cr,V)Si$_2$ phase as a function of the vanadium content (Fig. 2.11) shows a monotonic increase from pure CrSi$_2$ (x(V) = 0, $T_m = 1439 \, ^\circ$C) to pure VSi$_2$ (x(V) = 0.333, $T_m = 1682 \, ^\circ$C). This agrees with the expected trend from thermal analysis of the (Cr,V)Si$_2$ phase in Section 2.3.1 Part II (Fig. 2.4). However, the rate of increase in the melting temperature as predicted from the calculation is much more rapid than that experimentally measured (specifically for smaller additions of V). At V contents of 3.33 at. % and 6.66 at. %, the melting temperatures are calculated to be 1515 °C and 1557 °C, respectively. Both of these values are about 60 °C higher than those experimentally measured for the same compositions (1455 °C and 1499 °C), thus underscoring the need to achieve better homogeneity of the (Cr,V)Si$_2$ specimens (e.g. by extended annealing) for more reliable thermodynamic data of the phase. This, in turn, will allow for a more critical assessment of the thermodynamic parameters for the (Cr,V)Si$_2$ phase, including the determination of $^\circ L_{Cr,V} \, ^\circ(T)$ interaction parameters which are currently undefined.

![Figure 2.11: Calculated liquidus temperature of (Cr,V)Si$_2$ as a function of the vanadium content.](image)

The liquidus temperature of (Cr,V)Si$_2$ is shown in consistently increase from 1439 °C (for CrSi$_2$) to 1677 °C (for VSi$_2$) as vanadium is substituted for chromium.
To determine the Si-CrSi₂-VSi₂ eutectic boundary curve, a monovariant line with the liquid phase was calculated within the ternary phase region. In Fig. 2.12, this monovariant line (marked in red) is plotted over the experimentally investigated alloy compositions (from Fig. 2.5), with the determined eutectic boundary compositions (see Fig. 2.9) denoted by blue triangles. It is shown that the experimental eutectic points lie extremely close to the calculated curve, indicating the success of the thermodynamic parameters for the binary Si-CrSi₂ and Si-VSi₂ systems to be extrapolated into the ternary composition field. In fact, the largest discrepancy between the two sets of data is for the binary Si-CrSi₂ binary eutectic point (e₂), which differed from the calculated point by 2.5 at. % Si (as discussed in Section 2.3.2 Part I). In the next section, the use of this diagram to determine equilibrium solidification paths for specific alloy compositions will be explained.

**Figure 2.12:** The calculated eutectic boundary curve (red line) is plotted with the experimentally investigated alloy compositions (the blue triangles denoting the compositions identified as eutectic boundary points in Section 2.3.1 Part III). Excellent agreement between the calculated and experimental eutectic curves demonstrates the self-consistency of the thermodynamic parameters used to describe the Si-CrSi₂-VSi₂ system.
2.4 Discussion

2.4.1 Simulation of equilibrium solidification paths

As discussed in the beginning of this chapter, one of the most important applications of the phase diagram is the simulation of alloy solidification during processing. Of particular importance to the casting of anomalous eutectic alloys, such as Si-(Cr,V)Si₂, is the prediction of the primary phase fraction and the volume fraction of minor phase [(Cr,V)Si₂ in this case] formed during solidification – both of which have a significant effect on the resulting microstructure, and hence mechanical properties, of the alloys. In order to elucidate this point, equilibrium solidification paths were simulated for specific alloy compositions that were used during fracture (Chapter 3) and wear (Chapter 4) experiments. Comparison of actual alloy microstructures to these predictions are made in each of the respective chapters, along with a discussion of how microstructural features such as primary grains and volume fraction of the minor phase affect the mechanical performance of in-situ toughened Si-(Cr,V)₂ alloys. In Fig. 2.13, the alloy compositions for the fracture (red diamonds) and wear (purple downward triangles) studies are plotted with the experimental and calculated eutectic boundary curves determined for the Si-CrSi₂-VSi₂ system. The alloy compositions used for the fracture experiments correspond to the two binary eutectic compositions (alloys A and D) and two ternary eutectic compositions (alloys B and C) as determined from the thermal analysis presented in this chapter. The alloy compositions used for the wear experiments (alloys E-H) are all off-eutectic alloy compositions. In Chapters 3 and 4, the experimental alloy compositions will be referred to by these assigned letter designations.
Figure 2.13: The alloy compositions used in the fracture (Ch. 3) and wear (Ch. 4) studies are plotted with the experimental and calculated eutectic points determined for the Si-CrSi$_2$-VSi$_2$ system. Equilibrium solidification paths were simulated for each of these compositions so that they could be compared with actual microstructures observed for cast Si-(Cr,V)Si$_2$ alloys.

Examples of calculated solidification paths (Fig. 2.14) demonstrate the types of phase evolutions expected during equilibrium solidification of Si-(Cr,V)Si$_2$ alloys depending on their nominal composition with respect the relevant eutectic point or the eutectic boundary curve. For binary alloys A (Fig. 2.14a) and D (Fig. 2.14b) which were both found to be hypereutectic (i.e. Si-rich) with respect to the respective calculated Si-VSi$_2$ and Si-CrSi$_2$ eutectic points, a large fraction of primary Si is predicted to form ($V_{f}^{\text{primary}} \approx 17\%$ in each case) prior to eutectic solidification. Also, the volume fraction of the disilicide phase is much higher for alloy D ($V_{f}^{\text{VSi}} = 36.9\%$) than for alloy B ($V_{f}^{\text{VSi}} = 12.0\%$), as expected from the tie-line calculations performed in Chapter 1 for the different silicon-disilicide eutectic reactions (Table 1.5). Alloy C, which lies slightly to the left of the eutectic boundary curve (Fig. 2.13), is predicted to undergo a small amount ($V_{f}^{\text{primary}} \approx 2.6\%$) of primary (Cr,V)Si$_2$ solidification (Fig. 2.14c). Alloy G, which lies to the right of the eutectic boundary curve (Fig. 2.13), is predicted to undergo primary Si solidification.
\( V_{primary} \approx 8.9 \% \) (Fig. 2.14d). One important difference between the solidification patterns of the binary and ternary Si-(Cr,V)Si\(_2\) alloys is that concurrent nucleation of the silicon and disilicide phases can occur before the last liquid solidifies for the ternary alloys, but not for the binary alloys (i.e. eutectic solidification is univariant (\( F=1 \)) as opposed to invariant (\( F=0 \)), where \( F \) is the degrees of freedom of the system). The additional degree of freedom (\( F = C-P+1 \) for constant pressure) associated with moving from a binary to a ternary system in this case is due to the presence of a third component (\( C = 2 \rightarrow 3 \)) without the formation of an additional phase (\( P = 3 \) in both cases) since CrSi\(_2\) and VSi\(_2\) are completely soluble in one another. This difference is seen by comparing Figs. 2.14a,b (for the binary alloys) with Figs. 2.14c,d (for the ternary alloys). In the first two cases, nucleation of the disilicide phase does not occur until the fraction of liquid goes to zero. However, for the latter two alloys, both phases begin to form well before the fraction of liquid reaches zero. Thus, the presence of a univariant eutectic boundary curve tends to reduce the extent of primary solidification for off-eutectic alloy compositions. The fraction of primary solidification and disilicide content calculated for all of the alloys (A-H in Fig. 2.13) are listed in Table 2.2 (note that all of the compositions have been converted into wt. % since those are the compositions referred to in the latter chapters).
Figure 2.14: Simulated equilibrium solidification paths for four of the Si-(Cr,V)Si$_2$ alloys that were experimentally investigated in Chapter 3 and 4. Binary alloys (a) A and (b) D undergo a large degree of primary solidification prior to reaching the invariant eutectic reaction. Ternary alloys (c) C and (d) G undergo univariant eutectic solidification after some degree of primary (Cr,V)Si$_2$ and Si solidification, respectively. (See Fig. 2.13 for alloy letter designations).
Table 2.2: Calculated fractions of primary solidification and disilicide content for experimentally investigated Si-(Cr,V)Si$_2$ alloys in Chapter 3 (alloys A-D) and Chapter 4 (alloys E-H)

<table>
<thead>
<tr>
<th>Alloy Designation</th>
<th>Alloy Composition (wt. %)</th>
<th>$V_f^{\text{primary}}$ (%)$^*$</th>
<th>$V_f^{\text{MSi}_2}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Si: 93.00, Cr: 0.00, V: 7.00</td>
<td>17.1 [Si]</td>
<td>12.0</td>
</tr>
<tr>
<td>B</td>
<td>Si: 87.24, Cr: 7.72, V: 5.04</td>
<td>1.0 [(Cr,V)Si$_2$]</td>
<td>22.3</td>
</tr>
<tr>
<td>C</td>
<td>Si: 82.68, Cr: 13.91, V: 3.41</td>
<td>2.6 [(Cr,V)Si$_2$]</td>
<td>30.9</td>
</tr>
<tr>
<td>D</td>
<td>Si: 79.71, Cr: 20.29, V: 0.00</td>
<td>16.6 [Si]</td>
<td>36.9</td>
</tr>
<tr>
<td>E</td>
<td>Si: 91.20, Cr: 2.33, V: 4.74</td>
<td>5.2 [Si]</td>
<td>15.2</td>
</tr>
<tr>
<td>F</td>
<td>Si: 86.18, Cr: 11.27, V: 2.55</td>
<td>12.9 [Si]</td>
<td>24.4</td>
</tr>
<tr>
<td>G</td>
<td>Si: 81.40, Cr: 17.60, V: 1.00</td>
<td>8.9 [Si]</td>
<td>33.6</td>
</tr>
<tr>
<td>H</td>
<td>Si: 78.33, Cr: 21.67, V: 0.00</td>
<td>10.6 [Si]</td>
<td>39.5</td>
</tr>
</tbody>
</table>

$^*$ Primary phases are indicated inside brackets

2.4.2 Calculation of liquidus projections

Liquidus projections for the region near the Si-CrSi$_2$-VSi$_2$ eutectic boundary were determined through isothermal calculations for the liquid phase. To give a general comparison between the calculated and experimental liquidus temperatures, the liquidus projections are overlayed on top of the experimental compositions which are colored according to the range of temperatures within which the melting temperature was measured (Fig. 2.15). Good agreement between the calculated and experimental liquidus temperatures is indicated by the tendency of the measured liquidus temperatures (denoted by the colored shading in the experimental points) to fall between the corresponding colored liquidus lines for that temperature range. A more direct compassion can be made by using the actual melting temperatures for the experimental points in Tables B.4-B.9 of the appendix. The good agreement between the calculated and experimental liquidus curves is another confirmation of the self-consistency of the thermodynamic description for the Si-CrSi$_2$-VSi$_2$ system (Table B.1 of the appendix).
Figure 2.15: Isothermal lines (solid colored lines) calculated for the Si-CrSi$_2$-VSi$_2$ system in the region near the eutectic boundary curve. The colored shading in the experimental data points indicates the temperature range within which the melting point was measured. Satisfactory agreement between the measured melting points and the calculated liquidus curves is indicated by the tendency of the measured melting temperatures to fall between the corresponding colored liquidus lines for that temperature range. This agreement is another good indicator of the self-consistency of the thermodynamic parameters used to describe the Si-CrSi$_2$-VSi$_2$ system.
2.5 Concluding Remarks

Experimental determination of the Si-CrSi$_2$-VSi$_2$ was performed using calorimetric experiments supported by complimentary microstructural analysis. In particular, the binary Si-CrSi$_2$ and Si-VSi$_2$ binary eutectic compositions were identified, along with the eutectic boundary curve connecting these two invariant points. This experimental construction of the phase diagram was then compared with a predicted diagram computed using the CALPHAD method. Descriptions of the lattice stabilities (i.e. Gibbs energies) and interaction parameters for the various phases were taken from current optimizations of the Si-V system by Zhang et al. [141] and of the Si-Cr system by Du et al. [142], with the modification that (Cr,V)Si$_2$ was modeled as a single phase (see Table B.1). Good agreement between measured and calculated diagram features such as the eutectic boundary curve and liquidus projections indicate the self-consistent nature of the thermodynamic parameters used to describe this system. The present database, therefore, provides an invaluable tool for the processing of in-situ toughened Si-(Cr,V)Si$_2$ alloys, including the prediction of the phase volume fractions and the amount of primary solidification that occurs during processing – both calculations of which have been performed in the present chapter (assuming equilibrium conditions) for the different alloy compositions studied in Chapters 3 and 4.
Chapter 3: Microstructural effects on the long-crack behavior of in-situ toughened Si-(Cr,V)Si$_2$ alloys

3.1 Alloy and process design

3.1.1 Role of alloy composition on microstructural toughening in eutectic Si-(Cr,V)Si$_2$ alloys

As discussed in Chapter 2, the volume fraction of the reinforcing disilicide [(Cr,V)Si$_2$] in eutectic-based Si-(Cr,V)Si$_2$ alloys phase can be controlled by varying the alloy compositions along the eutectic boundary curve between the binary Si-VSi$_2$ and Si-CrSi$_2$ eutectic points. This is extremely important since the reinforcement volume fraction has a major effect on the degree of microstructural toughening that can be attained through the crack deflection and bridging mechanisms which are expected to be observed in Si-(Cr,V)Si$_2$ alloys (Sections 1.4.1 and 1.4.2). Furthermore, the alloy composition has major effects on some of the microstructural and morphological aspects of the in-situ composites (i.e. primary grains and eutectic morphology), which have implications for the effectiveness of the microstructural toughening mechanisms displayed by these materials (Section 1.4.2). Therefore, one focus of this chapter is to investigate the role of the eutectic composition on controlling the microstructure and morphology of Si-(Cr,V)Si$_2$ alloys and its influence on the fracture property of the these in-situ composites.

3.1.2 Role of processing on the microstructural evolution of die cast Si-(Cr,V)Si$_2$ alloys and the ensuing fracture properties

The eutectic boundary curve located within the Si-CrSi$_2$-VSi$_2$ system (Chapter 2) was established as a means to define the locus of alloy compositions which should provide for fully (or near fully) eutectic microstructures, and thus optimal fracture toughness values. The eutectic compositions determined in the previous chapter are based on the assumption of equilibrium solidification conditions. During most conventional casting processes, however, rapid solidification rates lead to non-equilibrium conditions and, as a result, variation of the microstructure throughout the as-cast alloy. Additionally, non-uniform, multidirectional temperature gradients can lead to variations in the characteristic spacing of eutectic alloys – even
within the same region of the casting. Thus, in addition to alloy composition, this chapter will also explore the effects of processing conditions on the microstructural evolution during casting of Si-(Cr,V)Si₂ alloys and their effects on the anisotropy of the alloys’ fracture properties.

### 3.2 Experimental Procedures

#### 3.2.1 Alloy preparation

Four alloys, whose compositions were found to lie on (or close to) the Si-CrSi₂ – Si-VSi₂ eutectic boundary curve (Chapter 2), were die cast using a vacuum induction melting process (Sophisticated Alloys Inc. Butler, PA). The alloy designations and compositions are listed in Table 3.1. The alloys are listed by increasing volume fraction of disilicide phase expected to be present in microstructure, with alloys A and D representing binary Si-VSi₂ and Si-CrSi₂ alloys, respectively. The raw materials used to produce these alloys consisted of large pieces of 99.98 wt. % Si chunks, 99.96 wt.% Cr pellets, and 99.86 wt.% V chips. All alloys (except alloy C) were melted in graphite crucibles (25.4 cm OD x 21.59 cm ID x 22.86 cm deep (25.4 cm high), GR030⁶) and poured into 0.03 m³ graphite molds (GM-111⁷) using a 136 kg capacity induction vacuum furnace. Alloy C was melted in a graphite crucible (15.24 cm OD x 11.43 cm ID x 22.86 cm deep (15.24 cm high), GR030). All alloys were poured into the graphite molds using a 136 kg capacity induction vacuum furnace.

<table>
<thead>
<tr>
<th>Alloy Designation</th>
<th>Alloy Composition (wt. %)</th>
<th>( V_{f}^{MSi_2} (%) )^*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>93.00 0.00 7.00</td>
<td>12.0</td>
</tr>
<tr>
<td>B</td>
<td>87.24 7.72 5.04</td>
<td>22.3</td>
</tr>
<tr>
<td>C</td>
<td>82.68 13.91 3.41</td>
<td>30.9</td>
</tr>
<tr>
<td>D</td>
<td>79.71 20.29 0.00</td>
<td>36.9</td>
</tr>
</tbody>
</table>

* \( V_{f}^{MSi_2} \) values are those theoretically predicted from the phase fraction calculations in Section 2.4.1 (Table 2.2).

---

⁶ GR030 and GM-111 refer to the grades of graphite used for the crucibles and molds, respectively. The GR030 is a fine grain extruded graphite and GM-111 is a very fine-grained, isostatically pressed graphite (further material properties can be found on the supplier’s site at https://www.graphitestore.com).
17.78 cm deep (20.32 cm high), GR030) and poured into a 0.01 m³ graphite mold (GM-111) using a 23 kg capacity induction vacuum furnace. The dimensions of the graphite molds are listed in Table 3.2. Prior to melting, the crucibles were baked at 540 °C for 30 min under vacuum (3 × 10⁻² torr) in the induction coil and were then cooled while still being pumped under vacuum. The graphite molds were baked in an oven (air atmosphere) at 430 °C for 45 min and then fan cooled before loading into the vacuum induction melter. Once the raw materials were loaded into the crucible, the vacuum chamber was evacuated to 5 × 10⁻⁵ torr and backfilled with 25" Hg argon prior to melting. The vacuum level was reached using two 10" diffusion pumps backed by roots blowers and rotary piston pumps. The pour temperature was estimated as 1550 °C and each pour took about 15 minutes once the chamber was pumped down. The melts were allowed to cool for one hour prior to opening the chamber. Slight taper on the walls of the graphite molds allowed for easy removal of the castings after solidification.

<table>
<thead>
<tr>
<th>Alloy(s)</th>
<th>Outside Length (cm)</th>
<th>Inside Length (cm)</th>
<th>Outside Width (cm)</th>
<th>Inside Width (cm)</th>
<th>Height (cm)</th>
<th>Depth (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A, B, D</td>
<td>43.18</td>
<td>33.02</td>
<td>22.86</td>
<td>12.70</td>
<td>16.51</td>
<td>11.43</td>
</tr>
<tr>
<td>C</td>
<td>20.96</td>
<td>17.15</td>
<td>12.70</td>
<td>8.89</td>
<td>6.99</td>
<td>5.08</td>
</tr>
</tbody>
</table>

3.2.2 Mechanical Testing

Long-crack toughness measurements for the Si-(Cr,V)Si₂ alloys were performed using four-point chevron-notched bend (CNB) tests according to the ASTM C 1421 standard [145]. Chevron-notched bars were cut and precision machined (Bomas Machine Specialties, Inc. Somerville, MA) from the Si-(Cr,V)Si₂ castings (Section 3.2.1) using the test geometry A [145] with bar dimensions of 50 mm x 3 mm x 4 mm [length (L) x width (B) x thickness (W)] and chevron notches with dimensionless tip positions (α₀ = a₀/W) of 0.20 and dimensionless base positions (α₁ = a₁/W) greater than or equal to 0.95 (Fig. 3.1). This geometry was used because it has been found to exhibit the most relative stable crack extension to maximum load, which allows for a near steady-state fracture toughness to be realized for rising R-curve materials [146]. It also
produces the lowest crack velocity for a given displacement rate, which eases the detection of stable crack propagation. [147]. All specimen dimensions were verified by measuring the beam dimensions with an electronic micrometer (± 1.0 μm) and the notch dimensions using secondary electron imaging (± 1.0 μm) with a LEO VP 438 SEM operating at an accelerating voltage of 20 kV. Specimens were machined in different orientations with respect to the castings as illustrated in Fig. 3.2. For alloys A, B, and D, specimens were machined in orientation 1. Attempts were made to machine all of the specimens from the same, central region of each casting so that the processing conditions were similar between specimens from different alloys, and thus only the effects of alloy composition on the resulting microstructure (see Section 3.2.3) and mechanical response of the composites could be analyzed. Due to the smaller mold dimensions, and thus thickness, of alloy C (Table 3.2), the specimens from this casting were unable to be machined in orientation 1, and were instead machined in orientation 2.

To understand the effects of processing conditions on the resulting microstructure, and hence fracture properties, of Si-(Cr,V)Si₂ alloys, additional CNB specimens were made for alloy D in all three orientations from the side regions of the casting which solidified near the mold walls. Solidification growth velocities in these regions are expected to be much greater than in the central region of the casting. For anomalous eutectic alloys, such as Si-(Cr,V)Si₂, increased growth velocities can cause frequent overgrowth of the non-faceted phase or a change in the growth mechanism of the faceted phase [118]. The effects of these changes in eutectic growth
Figure 3.2: Different orientations used for machining of CNB specimens. For the alloy D CNB specimens machined from the sides of the casting, the notches in orientations 1 and 2 were machined perpendicular to one of the preferred disilicide growth directions, whereas notches in orientation 3 were machined parallel to both of the preferred growth directions.

on the resulting fracture properties of the composites was analyzed. Also, based on the graphite mold dimensions (Table 3.2), the most rapid solidification growth directions (which correspond to the directions of maximum heat extraction from the molds) are those perpendicular to the outer/inner side (length x height/depth) and bottom (length x width) mold walls. These rapid growth directions correspond to the preferred disilicide growth orientations. Thus, specimens machined in orientations 1 and 2 have notch (or crack) planes oriented perpendicular to at least one of the preferred disilicide growth directions, whereas specimens machined in orientation 3 have notch planes oriented parallel to both growth directions (Fig. 3.2). The effect of disilicide orientation on the fracture toughness of Si-(Cr,V)Si₂ alloys (with the same composition) was also studied.

Two different custom four-point bend test fixtures were used for the CNB tests (Fig. 3.3). Both fixtures used outer (So) and inner (Si) spans of 40 mm and 20 mm, respectively, and steel dowel pins with a diameter of 4.5 ± 0.5 mm and length of 12.5 ± 0.5 mm. The fixture in Fig. 3.3a was used in conjunction with an Instron 5500R mechanical tester in compression mode. A crosshead cylinder was used to push down the inner span fixture, which was guided by slats, at a rate of 0.06 mm/min. A 890 N load cell (200 lbf) with a resolution of ± 10 μN (located under the stage of the Instron) was used to capture data every 0.1 sec. This allowed for very accurate detection
of either a smooth (nonlinear) transition through the maximum load or a pop-in event followed by a subsequent force increase to the maximum load prior to failure (see Section 3.3.1). Each of these behaviors is a signature of stable fracture prior to failure – a necessary condition for valid chevron-notched beam tests. Some specimens were unloaded prior to complete fracture (but after the maximum load was reached) and others were allowed to break so that fractographic images of the crack plane could be taken in both longitudinal and transverse directions, respectively. The fixture in Fig. 3.3b was used for in-situ CNB testing inside of an SEM (LEO VP 438). A 50 N compression load cell (OMEGA LCMKD-50N) was placed behind the inner span of the four-point fixture. A custom-written operating program (Microsoft Visual Basic 6.0) drove a HURST PBS 3208-004 geared stepper motor (at 1 μm/sec) which pushed the inner span fixture (including load cell) against the test specimen. The program collected force data by actively linking to data (which was acquired from the load cell) using a Dataq Instruments DI-718B data acquisition system with a DI-8B38-32 30 mV strain gauge bridge module and Windaq/Lite data acquisition software. The motor was stopped at different load intervals to

Figure 3.3: Chevron-notched four-point bend test fixtures used for the (a) Instron test method and (b) in-situ test method with an SEM. The fixture in (a) was used to obtain high resolution force vs. displacement data, while the fixture in (b) was used to image crack propagation during CNB testing.
capture images of the notch region (and advancing crack) using back-scattered electron imaging at an accelerating voltage of 20 kV. This allowed real-time observation of the crack’s propagation and its interactions with the alloy microstructures. Also, the total crack extension was measured to correlate with the long-crack toughness values, and thus provide the crack extensions which are associated with the upper part of the R-curve for these alloys. To ensure the validity of fracture toughness results, CNB tests (using the fixture in Fig 3.3a) were also performed on 99.999 wt.% silicon (Alfa Aesar Ward Hill, MA) and commercial Hexoloy® SA silicon carbide (Saint-Gobain Ceramics Niagara Falls, NY); the latter of which fracture toughness values have been measured using the CNB method [147-149], as well as disk-shaped compact-tension (DC(T)) and controlled-surface-flaw methods [150].

For all CNB tests, the fracture toughness ($K_{Ivb}$) was calculated using the following equation:

$$K_{Ivb} = Y_{min}^* \left( \frac{P_{max} (S_o - S_i) \times 10^{-6}}{BW^{3/2}} \right)$$

(3.1)

where $P_{max}$ is the relevant maximum load and $Y_{min}^*$ is the stress intensity factor coefficient. The stress intensity factor coefficient was calculated using the expressions derived from the straight-through-crack-assumption [147]. Such expressions have been found to be good approximations of the stress intensity factor coefficient for specimen geometries with $\alpha_1 \approx 1$ [147]. For each set of specimens, both the range of values and average value for $K_{Ivb}$ are reported.

### 3.2.3 Microstructural characterization

Microstructural analysis was performed on the mechanically tested CNB specimens (Section 3.2.2) using a combination of scanning electron microscopy and energy dispersive spectroscopy (EDS) techniques. For each set of test specimens, three broken beams were sectioned at a distance of about 2-3 mm behind the notch plane. The plane parallel to the notch was metallographically prepared by grinding and polishing down to a 0.06µm finish using a MasterMet® colloidal silica suspension. Each of the alloys was characterized by its eutectic morphology and the volume fraction of disilicide phase. The eutectic morphology was
characterized based on the classification scheme described in Section 1.4.2 Part II-E. The volume fraction of the disilicide phase was determined using an imaging segmentation process (with EDS 2004 v1.3 software) on back-scattered SEM images. These values were compared to the phase fraction calculations shown in Table 3.1. The segmentation process uses the contrast in signal intensities (or brightness) of different phases to create a color coded map of the different phase regions and calculate their respective area, or equivalently, volume fractions. To provide a physical reasoning for the range of fracture toughness values measured for each alloy, the local microstructure surrounding the notches of specimens displaying the highest and lowest fracture toughness values from their respective alloy set was analyzed. The eutectic spacing was measured in these notch regions using a linear intercept procedure [151]. Such an analysis was to provide valuable insight into the effects of local microstructural fluctuations (due to solute segregation) on the variation of the fracture properties of Si-(Cr,V)Si$_2$ in-situ composites processed using multidirectional solidification techniques. All SEM images were taken on a LEO VP 438 SEM operating at an accelerating voltage of 20 kV.

### 3.3 Experimental Results

#### 3.3.1 Microstructural analysis

Figure 3.4 shows an example of how back-scattered electron micrographs of the Si-(Cr,V)Si$_2$ alloys (Fig. 3.4a) were transformed into segmentation images (Fig. 3.4b) which were used to determine the volume fractions of the different phases in the Si-(Cr,V)Si$_2$ alloys. In this case, the volume fraction of silicon is equal to the portion of the image colored in green, while the volume fraction of the disilicide phase is that portion colored in blue. The volume fractions of (Cr,V)Si$_2$ measured for alloys A-D in this manner are listed in Table 3.3 along with the calculated volume fractions (reproduced from Table 3.1). For alloy D, measurements are given for both the specimens machined from the center of the casting and from the sides of the casting (for the latter, the volume fraction was taken as the average from all three notch orientations). In most cases, the measured (Cr,V)Si$_2$ volume fraction was around 2-7 % lower than that expected from the equilibrium solidification calculations. This is mainly due to microstructural variations from solute segregation during non-equilibrium solidification. During the casting process, rapid
Figure 3.4: (a) Back-scattered electron images of the Si-(Cr,V)Si₂ alloys (alloy D shown here as an example) were used to create (b) segmentation images to determine the volume fraction of the individual phases composing the microstructure. The silicon phase is colored in green and the disilicide phase is colored in blue.

Solidification rates prevent any substantial diffusion in the solid from occurring. Under such conditions, the rejection of solute into the liquid during primary solidification (for off-eutectic alloys) gives rise to a concentration gradient in the casting, with the last liquid to solidify reaching the eutectic composition. These compositional gradients can cause both global and local variations of the microstructure throughout the casting and thus differences in volume fraction measurements from one area to the next. This is clearly seen by comparing the two sets of alloy D specimens machined from different regions of the casting. Specimens machined from the center of the casting (last region to solidify) were measured to have a significantly higher volume fraction of (Cr,V)Si₂ than those machined from the sides of the casting (first region to solidify).

Table 3.3: Experimental versus calculated disilicide volume fractions

<table>
<thead>
<tr>
<th>Alloy Composition (wt %)</th>
<th>% (Cr,V)Si₂ (exp.)</th>
<th>% (Cr,V)Si₂ (calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-7.00V (Alloy A)</td>
<td>6.68 ± 0.9</td>
<td>12.0</td>
</tr>
<tr>
<td>Si-7.72Cr-5.04V (Alloy B)</td>
<td>19.86 ± 0.8</td>
<td>22.3</td>
</tr>
<tr>
<td>Si-13.91Cr-3.41V (Alloy C)</td>
<td>23.82 ± 0.9</td>
<td>30.9</td>
</tr>
<tr>
<td>Si-20.29Cr (Alloy D) – center</td>
<td>39.61 ± 2.3</td>
<td>36.9</td>
</tr>
<tr>
<td>Si-20.29Cr (Alloy D) – sides</td>
<td>31.33 ± 7.1</td>
<td>36.9</td>
</tr>
</tbody>
</table>
Alloys A-D were observed to display different types of anomalous eutectic microstructures. Alloy A (Fig. 3.5) displays mostly a fibrous structure (with some unbranched plates) which is made up of small, rod-like disilicide particles. Fibrous morphologies tend to be stable for minor phase volume fractions below about 0.10, which is what was measured for this particular alloy (Table 3.3). Some of the disilicide fibers were found to be tubular in nature, containing silicon-filled pores in the center of the rods (Fig. 3.5b). As the volume fraction of (Cr,V)Si$_2$ is increased in alloy B, the microstructure becomes an irregular structure composed of massive branched and unbranched plates of the (Cr,V)Si$_2$ phase (Fig.3.6). Alloy C, which has a measured volume fraction of (Cr,V)Si$_2$ slightly greater than 0.20, is shown to exhibit mostly an irregular branched-plate type structure with a small amount of complex-regular structure appearing as small, island-like clusters (Fig. 3.7). This microstructure is similar to that of alloy B, except that the arrangements of plates are regular over larger areas. Alloy D specimens machined from the center of the casting (Fig. 3.8) were observed to have undergone quasi-regular growth, resulting in a pseudo-colony type structure in which the disilicide phases have a high degree of alignment about a particular growth direction. Such a structure is common starting at a minor phase volume fraction of about 0.40, which was around that measured in the center of the casting. The eutectic structure becomes coarse and irregular at the colony boundaries (Fig. 3.8b) due to the cumulative effects of branching and coalescence of the minor phase near the boundary.

Figure 3.5: Alloy A ($V_f = 6.7\%$) is shown to have a fibrous microstructure with some unbranched plates. The SEM micrograph in (b) is a magnified view of the microstructure shown in (a). (SEM images were taken using back-scattered imaging)
Figure 3.6: Alloy B ($V_f = 19.9\%$) has an irregular structure composed of massive branched and unbranched plates. The SEM micrograph in (b) is a magnified view of the microstructure shown in (a). (SEM images were taken using back-scattered imaging)

Figure 3.7: Alloy C ($V_f = 23.8\%$) has a mostly an irregular branched-plate structure with some complex regular structure. The SEM micrograph in (b) is a magnified view of the microstructure shown in (a). (SEM images were taken using back-scattered imaging)
Figure 3.8: Alloy D ($V_f = 39.6\%$) specimens machined from the center of the casting display quasi-regular growth which consists of a pseudo-colony type structure with high alignment of the disilicide phases about a specific growth direction. The SEM micrograph in (b) is a magnified view of the microstructure shown in (a). (SEM images were taken using back-scattered imaging)

Back-scattered electron micrographs of the alloy D specimens machined from the sides of the casting are shown in Fig. 3.9 for each of the different notch orientations. For the specimens machined in orientation 1 (Fig. 3.9a,b), a similar colony type structure is observed as for the alloy D specimens machined in the same orientation from the center of the casting (Fig. 3.8). However, increased growth velocities near the mold walls caused overgrowth of the non-faceting silicon phase in this region of the casting, resulting in extremely large silicon regions being present in the microstructure. Overgrown silicon regions are also seen from the specimens having notch orientations of type 2 (Fig. 3.9c,d) and type 3 (Fig. 3.9e,f). A close examination of the eutectic structure within the colonies reveals that a higher fraction of the disilicide lamellae grew in a direction nearly perpendicular to the notches cut in orientations 1 (Fig. 3.9b) and 2 (Fig. 3.9d) than those cut in orientations 3 (Fig. 3.9f). This is in agreement with the expectations of the preferred disilicide growth directions based on the geometry of the molds from which the alloys were cast (Fig. 3.2).
Figure 3.9: Alloy D ($V_f = 31.3\%$) specimens machined from the sides of the casting display the same colony type structure as the specimens machined from the center of the same casting (Fig. 3.8). Overgrowth of the silicon phase has occurred in this region of the casting due to the more rapid solidification rates near the mold walls from where these specimens were machined. With respect to Fig. 3.2, the micrographs were taken from notch planes of orientation (a,b) type 1, (c,d) type 2, and (e,f) type 3 (where (b), (d), and (f) and are magnified views of the microstructures shown in (a), (c), and (e), respectively). A higher fraction of the disilicide lamellae grew in a direction nearly perpendicular to the notches cut in orientations 1 and 2 than those cut in orientations 3. (SEM images were taken using back-scattered imaging)
3.3.2 Chevron-notched beam fracture tests

Load-extension curves for the reference unalloyed silicon specimens (Fig. 3.10a) showed a consistent linear increase in load followed by a sudden load drop at the failure point. This response is indicative of crack initiation away from the chevron tip (due to test specimen overload) and subsequent unstable fracture. Smooth fracture surfaces with ridges extending from the chevron tip were observed in transverse images of the notch planes after failure (Fig. 3.10b). In addition, longitudinal images (Fig. 3.10c) of the notch planes revealed an extremely tortuous crack propagation path; thus, confirming that unstable fracture occurred in the silicon specimens and that the $K_{Ivb}$ measurements for this material were invalid. Similar difficulties in achieving stable crack propagation in CNB specimens of brittle materials have been reported for soda-lime-silica glass and vitreous silica [152] which have fracture toughness values ($K_{fc} = 0.75 – 0.80$ MPa·m$^{1/2}$) close to that of silicon. Hexoloy® SA SiC (Fig. 3.11a), on the other hand, exhibited pop-in prior to reaching the maximum load which indicates that a sharp crack was initiated at the chevron tip and that the tests on this material were valid. A fracture toughness of $2.88 \pm 0.04$ MPa·m$^{1/2}$ was measured for Hexoloy® SA SiC which is in good agreement with the values measured by Jenkins et al. (2.91 ± 0.29 MPa·m$^{1/2}$) [149] Salem et al. (2.61 ± 0.05 MPa·m$^{1/2}$) [147] and Himsolt et al. (2.6 – 2.9 MPa·m$^{1/2}$) [148] using the CNB test method, as well as the value of 2.8 MPa·m$^{1/2}$ obtained by Gilbert et al. [150] using the controlled-surface-flaw method. Fractographic images of SiC test specimens revealed a better-behaved fracture pattern as noted by a smooth, flat fracture surface (Fig. 3.11b) and a straight crack path through the middle of the notch plane (Fig. 3.11c). A straight crack pattern and catastrophic failure at maximum load are both characteristic of materials, such as SiC [149, 150], that display single-value toughness (i.e. flat R-curve). Based on the ability to accurately detect stable fracture and the agreement of the fracture toughness values of Hexoloy® SA SiC with those cited in the literature, the Instron four-point CNB test apparatus (Fig. 3.3a) was deemed suitable for obtaining valid $K_{Ivb}$ fracture toughness measurements.
Figure 3.10: (a) Sudden load drops from the initial linear portion of the load-extension curves for unalloyed silicon CNB test specimens indicate unstable fracture due to overload, and thus invalid test data. (b) Fracture ridges extending from the chevron tip and (c) tortuous crack paths were observed in transverse and longitudinal fractographic images of the silicon notch planes, respectively. These images suggest extremely unstable crack initiation and propagation which is in agreement with the load-extension response of this material. (SEM images in (b) and (c) were taken using secondary and back-scattered imaging, respectively)
Figure 3.11: (a) Load-extension curves for Hexoloy® SA silicon carbide CNB specimens revealed pop-in followed by a subsequent load increase (stable fracture) to the maximum load at which point catastrophic failure occurred. A well-behaved fracture pattern in this material was noted by (b) flat, smooth fracture surfaces in transverse fractographic images of the notch plane, as well as by (c) straight crack propagation paths in longitudinal fractographic images of the notch plane. Such fracture behavior is characteristic of a material that displays single-value toughness (i.e. flat R-curve) and that fails in a catastrophic manner (as noted in the load-extension response). (SEM images in (b) and (c) were taken using secondary and back-scattered imaging, respectively)
An example of a typical load-extension response during CNB testing of the Si-(Cr,V)Si₂ composites is shown for alloy C (Fig. 3.12a) where after the initial pop-in and stable propagation of the crack, a smooth transition through the maximum load is observed. This is in contrast to both Si and SiC (Figs. 3.10a and 3.11a) which showed a sudden load drop after reaching the maximum load. Transverse images of the crack planes in Si-(Cr,V)Si₂ CNB specimens (Fig. 3.12b) show a very rough fracture surface with clear delamination occurring between the Si and (Cr,V)Si₂ phases. A high degree of crack deflection and crack bridging was also evident in longitudinal images of the notch planes of Si-(Cr,V)Si₂ intact specimens that were unloaded after reaching the maximum load, but prior to complete fracture (Fig. 3.12c). The non-catastrophic fracture response of the Si-(Cr,V)Si₂ alloys, as depicted by a gradual decrease in load after stable crack propagation from the pop-in (Fig. 3.12a), can thus be attributed to a rising R-curve behavior, or an increase in crack resistance with crack growth. The small perturbations in the maximum region of the load-extension curves most likely correspond to fracturing of the disilicide reinforcements within the bridging zone of the crack wake during propagation. Evidence of crack deflection and bridging agree with the predictions of weak interfaces between silicon and the disilicide phases due to high residual tensile stresses (Section 1.4.2 Part II-C).

Table 3.4 lists the fracture toughness values measured for each of the different alloys in the specified orientations and regions of casting from which the specimens were machined. The values in parenthesis for the average fracture toughness values indicate the number of valid measurements made for that specimen.

<table>
<thead>
<tr>
<th>Material</th>
<th>Orientation (Fig. 3.2)</th>
<th>Region of Casting</th>
<th>Avg. Fracture Toughness (MPa√m)</th>
<th>Min. Fracture Toughness (MPa√m)</th>
<th>Max. Fracture Toughness (MPa√m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>N/A</td>
<td>-</td>
<td>invalid</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hexoloy® SA SiC</td>
<td>N/A</td>
<td>-</td>
<td>2.88 ± 0.04 (4)</td>
<td>2.85</td>
<td>2.93</td>
</tr>
<tr>
<td>Alloy A</td>
<td>1</td>
<td>Center</td>
<td>2.06 ± 0.36 (7)</td>
<td>1.63</td>
<td>2.43</td>
</tr>
<tr>
<td>Alloy B</td>
<td>1</td>
<td>Center</td>
<td>2.26 ± 0.45 (11)</td>
<td>1.58</td>
<td>3.05</td>
</tr>
<tr>
<td>Alloy C</td>
<td>2</td>
<td>Center</td>
<td>2.34 ± 0.37 (10)</td>
<td>1.77</td>
<td>2.86</td>
</tr>
<tr>
<td>Alloy D</td>
<td>1</td>
<td>Center</td>
<td>invalid</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Alloy D</td>
<td>1</td>
<td>Sides</td>
<td>2.40 ± 0.22 (3)</td>
<td>2.14</td>
<td>2.55</td>
</tr>
<tr>
<td>Alloy D</td>
<td>2</td>
<td>Sides</td>
<td>2.61 ± 0.15 (4)</td>
<td>2.46</td>
<td>2.77</td>
</tr>
<tr>
<td>Alloy D</td>
<td>3</td>
<td>Sides</td>
<td>2.15 ± 0.13 (5)</td>
<td>2.02</td>
<td>2.26</td>
</tr>
</tbody>
</table>
Figure 3.12: (a) Load-extension curves for Si-(Cr,V)Si_2 CNB specimens revealed an initial pop-in followed by a load increase (stable crack propagation) with a smooth transition through the maximum load. (b) Transverse images of the crack planes of the Si-(Cr,V)Si_2 composites show a rough fracture surface with delamination between the Si and (Cr,V)Si_2 phases. (c) Longitudinal images of the crack planes after unloading of the CNB specimens once the maximum load was reached (but before complete fracture) demonstrates that fracture was controlled through crack deflection and bridging mechanisms. Both fractographic images support the predictions of weak interfaces between the silicon and disilicide phases due to residual tensile stresses as discussed in Chapter 1 (Section 1.4.2 Part II-C). Such fracture behavior is characteristic of a material that displays a rising R-curve and that fails in a non-catastrophic manner (as noted by the gradually decreasing portion of the load-extension curve). (SEM images in (b) and (c) were taken using back-scattered imaging)
From the data listed in Table 3.4, it is seen that all the Si-(Cr,V)Si₂ composites display fracture toughness values greater than 2 MPa·m¹/² which is over two times that cited for unalloyed silicon (~0.8 – 1.0 MPa·m¹/²), as noted from Tables 1.1 and 1.2. Comparison of the specimens machined from the center of their respective casting shows that the average fracture toughness increases from alloy A to C, which corresponds to an increase in the measured (Cr,V)Si₂ volume fraction (Table 3.3). No valid tests were able to be performed on specimens machined from the center of the alloy D casting (orientation 1), for which a high degree of disilicide alignment was observed (Fig 3.8). During CNB testing of these specimens, two types of fracture responses were found to occur. In the specimens where the (Cr,V)Si₂ reinforcements near the notch walls were aligned parallel to the crack direction, fracture only occurred near the sides of the notch plane (Fig. 3.13a). In the specimens where the (Cr,V)Si₂ reinforcements were aligned perpendicular to the crack direction, an extremely high degree of crack deflection and bridging resulted in the deflection of the crack out of the notch plane (Fig. 3.13b). While quantitative data cannot be accurately assessed in either case, the latter type of fracture behavior is suggestive of a relatively high fracture toughness compared to the other alloys with less well-aligned disilicide reinforcements. Valid tests were able to be performed for specimens machined from the side regions of the alloy D casting. These specimens show a dependence of the fracture toughness on the notch orientation, with the toughness being higher for those specimens machined with the notch oriented perpendicular to one of the preferred disilicide growth directions (i.e. orientations 1 and 2 as shown in Fig. 3.2). It should be pointed out that some of the specimens machined from the side regions also displayed the same types of fracture behavior as shown in Fig. 3.13. Those specimens that were able to be tested tended to have overgrown Si regions (seen in Fig. 3.9) around the notch tip (Fig. 3.14) which acted as low energy fracture paths, allowing crack propagation to proceed within the notch plane.

Compared to SiC, all of the Si-(Cr,V)Si₂ alloys display a much larger range in fracture toughness – a direct result of both the global and local variations in the alloy microstructure which were previously described. These microstructural effects can be observed in transverse images of the notch tip regions of those tested CNB specimens which displayed the highest and lowest fracture toughness values in the ranges cited in Table 3.4 for the various alloys (Fig. 3.15). In each of the specimens displaying the maximum toughness value (Fig. 3.15a-c), the microstructure
Figure 3.13: Two types of fracture responses observed during CNB testing of alloy D specimens machined from the center of the casting. (a) When the (Cr,V)Si₂ reinforcements near the notch walls were oriented parallel to the crack direction, fracture would occur only along those walls, away from the center of the notch. (b) When the (Cr,V)Si₂ reinforcements were oriented perpendicular to the crack direction, extensive crack deflection and bridging forced the crack completely out of the notch region. (SEM images were taken using back-scattered imaging)

Figure 3.14: Large silicon regions around the notch tips of alloy D CNB specimens machined from the sides of the casting provided low resistance paths of crack propagation to occur within the notch plane. This allowed for valid fracture toughness data to be obtained for these specimens. Shown here is a specimen machined with a notch orientation of type 1 (see Fig. 3.2). (SEM image was taken using back-scattered imaging)
surrounding the notch appears fully or near-fully eutectic and a high degree of crack deflection and bridging is observed. For those specimens displaying minimum toughness values (Fig. 3.15 d-f), large silicon regions (from overgrowth of the silicon phase) are present around the notch tip. These regions provide little fracture resistance during the initial stages of crack growth. Since no bridging zones form in the wake of the crack during the initial stages of crack growth, the stress intensity becomes too high for any eutectic structure present in the middle or base of the notch region to contribute any significant toughening. A more detailed discussion of the effects of Si overgrowth on the fracture properties of Si-(Cr,V)Si₂ composites is presented in Section 3.4.2.

In order to quantitatively compare the microstructures shown in Fig. 3.15, the disilicide spacing was measured (Table 3.5) in the notch planes for a distance of 1600 μm from the notch tip (a total of 5 measurements was taken from each specimen). As expected, the specimens displaying the maximum toughness for their respective alloy set had significantly smaller disilicide spacings than their counterparts displaying the minimum toughness – this difference being attributed to the large Si regions present in the latter specimens. Of course, the relationship between the fracture toughness and alloy microstructure is dependent on more than the disilicide spacing. For instance, comparison between only the toughest specimens from each alloy set demonstrates that even specimens containing very similar disilicide spacings (within experimental error) can display noticeably different fracture toughness values. In this case, the toughness is governed by microstructural features such as the volume fraction (Table 3.3), morphology (Figs. 3.5 – 3.7), and orientation or the reinforcing disilicide phase. For anamalous eutectic alloys, such as Si-(Cr,V)Si₂, these features are interdependent on one another, making the microstructural-mechanical property relationships for these materials more complex compared to normal eutectic structures (see Section 3.4.1 for further discussion).

<table>
<thead>
<tr>
<th>Specimen (see Table 3.4)</th>
<th>Fracture Toughness (MPa√m)</th>
<th>Disilicide Spacing (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy A (min)</td>
<td>1.63</td>
<td>70 ± 20</td>
</tr>
<tr>
<td>Alloy A (max)</td>
<td>2.43</td>
<td>36 ± 2</td>
</tr>
<tr>
<td>Alloy B (min)</td>
<td>1.58</td>
<td>88 ± 8</td>
</tr>
<tr>
<td>Alloy B (max)</td>
<td>3.05</td>
<td>39 ± 4</td>
</tr>
<tr>
<td>Alloy C (min)</td>
<td>1.77</td>
<td>41 ± 6</td>
</tr>
<tr>
<td>Alloy C (max)</td>
<td>2.86</td>
<td>30 ± 4</td>
</tr>
</tbody>
</table>
Figure 3.15: Transverse images of the notch regions for the CNB specimens that displayed (a-c) the highest and (d-f) the lowest fracture toughness values in the ranges cited for the various alloys (Table 3.4). In all of the notch regions of specimens displaying the maximum toughness value, a fully or near-fully eutectic structure is observed around the notch tip. On the other hand, large Si regions existed in the notch tip region for those specimens displaying minimum toughness values. (SEM images were taken using back-scattered imaging)
Crack-microstructure interactions during fracture in Si-(Cr,V)Si₂ alloys was observed through in-situ CNB testing of the Si-(Cr,V)Si₂ alloys. An example of this is shown in Fig. 3.16 by a collage of micrographs taken during in-situ testing of an alloy B specimen (the columns of micrographs going from right to left correspond to the regions A, B, and C, respectively, denoted in the top micrograph of the entire notch area). Visible pop-in of the crack from the notch tip (region A) occurs at a load of about 15N after at which point it extends about 200 μm into the notch plane. As the load is increased, the crack from the notch tip becomes bridged by the surrounding (Cr,V)Si₂ plates. At a load of 19.76 N, the crack propagates about 240 μm between regions A and B (first micrograph shown for region B). By the time the load reaches 22.46 N the crack has grown to a length of approximately 1460 μm into the beginning of region C. Meanwhile, the bridging area becomes larger, and significant crack-opening displacement can be observed in the bridging zone in the wake of the crack near the notch tip in region A. Complete failure of this particular specimen occurred after reaching a maximum load of 23.89N (K_{Ivb} = 2.54 MPa·m^{1/2}). The stable crack length reached about 1980 μm prior to failure [about 50x the characteristic microstructural spacing of this alloy (~ 40 μm)], which likely means the measured toughness value is in the upper region of the R-curve for this alloy. Using this type of in-situ analysis, the total measured crack growth (Δa) (and dimensionless crack growth (Δα = Δa/W = α – α₀), see Fig. 3.1), was measured using for one specimen of each alloy (Table 3.6). The load at which the corresponding maximum crack length measurement was made is also listed in Table 3.6 along with the actual failure load and calculated fracture toughness.

**Table 3.6:** Load-crack extension measurements made on Si-(Cr,V)Si₂ CNB specimens during in-situ testing.

<table>
<thead>
<tr>
<th>Material</th>
<th>Orientation (Fig. 3.2)</th>
<th>Total measured crack growth Δa (μm) [Δα = α-α₀]</th>
<th>Load at Δa (N)</th>
<th>Failure Load (N)</th>
<th>Fracture Toughness K_{Ivb} (MPa√m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy A</td>
<td>1</td>
<td>474 [0.12]</td>
<td>17.02</td>
<td>17.19</td>
<td>1.83</td>
</tr>
<tr>
<td>Alloy B</td>
<td>1</td>
<td>1976 [0.49]</td>
<td>23.89</td>
<td>23.89</td>
<td>2.54</td>
</tr>
<tr>
<td>Alloy C</td>
<td>1</td>
<td>518 [0.13]</td>
<td>17.51</td>
<td>18.69</td>
<td>1.99</td>
</tr>
<tr>
<td>Alloy D (center)</td>
<td>1</td>
<td>424 [0.11]</td>
<td>18.89</td>
<td>19.62</td>
<td>2.09</td>
</tr>
<tr>
<td>Alloy D (sides)</td>
<td>1</td>
<td>611 [0.15]</td>
<td>18.49</td>
<td>19.63</td>
<td>2.09</td>
</tr>
<tr>
<td>Alloy D (sides)</td>
<td>2</td>
<td>458 [0.11]</td>
<td>19.50</td>
<td>19.84</td>
<td>2.11</td>
</tr>
</tbody>
</table>
Figure 3.16: Collage of micrographs taken during the in-situ testing of alloy B. The column of micrographs on the right correspond to those taken from region A, those in the middle to region B, and those on the right to region C. (SEM images taken using back-scattered imaging)
According to the load-crack responses (Table 3.6), most of the Si-(Cr,V)Si₂ composites were found to fail after a total crack extension of 400 – 600 μm (Δα = 0.10 – 0.15). For those specimens in which the failure load was higher than the load at which the final crack extension measurement was made, the total crack extension is expected to be greater than the reported values. The measured crack extensions are in good agreement with those that are typically required to achieve the minimum stress intensity factor for the chevron notch A configuration [146]. Only the alloy B specimen was observed to achieve significantly higher crack extensions (4-5 times greater). The inability of the other specimens to display the same degree of crack extensions can be attributed to one or more of the sources associated with microstructural toughening in Si-(Cr,V)Si₂ composites: volume fraction of the disilicide phase, disilicide spacing, the eutectic morphology, orientation of the disilicide phase, and the presence of primary or overgrown Si regions. An interesting example of the effects of the disilicide orientation was found for the alloy D specimen machined from the center of the casting for which images were captured right at the point of complete fracture (Fig. 3.17). Observations of the notch plane (Fig. 3.17a) show that the microstructure of this specimen was fully eutectic, exhibiting the expected quasi-regular colony type structure of highly aligned disilicide ligaments (Fig. 3.8). Based on the high volume fraction of the disilicide phase (Vₐ = 39.6 %) and very fine eutectic spacing (λ ~ 5-6 μm) of this specimen compared to alloy B (Vₐ = 19.9 %, λ ~ 40 μm), one would expect a higher degree of microstructural toughening (based on crack bridging) to have occurred for alloy D. For this particular specimen, however, the orientation of the disilicide phase happened to be parallel to the crack direction – completely minimizing any potential toughening effects from crack bridging. A closer examination of the fracture surfaces near the notch tip (Fig. 3.17b) show that almost all of the disilicide reinforcements were, in fact, oriented parallel to the crack direction, resulting in very small deflections of the crack as it passed through the eutectic colony. On the other hand, the irregular structure of alloy B (Fig. 3.6), results in a higher fraction of the disilicide reinforcements to act as bridging ligaments during crack propagation, and thus contribute to the overall microstructural toughening achieved for this specimen (Fig. 3.17). A more detailed discussion of the effects of microstructure on the isotropy of fracture toughness in Si-(Cr,V)Si₂ composites will be presented in Section 3.4.1.
Figure 3.17: (a) Back-scattered electron micrograph of a fully eutectic alloy D specimen at the point of final fracture during in-situ CNB testing. (b) Magnified view of the chevron-notch tip region marked in (a) (by red rectangle) shows that nearly all of the disilicide reinforcements are aligned parallel to the direction of crack propagation, resulting in minimal initiation of the deflection and bridging toughening mechanism.

The load-crack extension curve for alloy B (Fig. 3.18) was used to estimate a lower-bound fracture toughness for alloy D specimens in cases where the eutectic colonies are oriented perpendicular to the crack direction (such as in Fig. 3.13b, where crack deflection out of the notch plane prohibited measurements by the conventional CNB testing method). To separate out the effects of the notch geometry and material properties, only the part of the crack extension governed primarily by the material’s R-curve was analyzed. This region was defined as the point at which a severe decrease in the slope of the load-crack extension curve was observed (denoted in Fig. 3.18 by dotted line), signaling that a transition through the minimum stress intensity
(Y_{min}^*) for had occurred. At this transition point, additional loading promotes fracture instability since the strain energy release rate is positive, and thus stable crack extension can only be supported by an increase in the material’s fracture toughness (i.e. a rising R-curve). A linear fit was made to the load-crack extension data within the unstable fracture region for alloy B (dotted blue line in Fig. 3.18). The data point corresponding to the load and crack extension at which the crack was deflected out of the notch of alloy D (Fig. 3.13b) is marked by the black square (it was presumed that the maximum load measured for this specimen corresponded with the deflection of the notch out of the plane). If it assumed that the slope of the load-crack extension lines in the unstable region are equal for alloy B and D (i.e. have the same R-curve behavior) and that the total amount of possible crack extension is the same in both specimens, then the load at which the alloy D specimen would fail if the crack remained in the notch plane (marked by open square) is predicted to be 27.06 N (K_{Ivb} = 2.88 MPa·m^{1/2}). This toughness is believed to be a lower bound estimate and that both the actual slope of the R-curve and degree of obtainable stable crack extension for alloy D is greater than that measured for alloy B (this being specifically for cases where alloy D has a completely eutectic microstructure with unidirectional disilicide reinforcements aligned perpendicular to the direction of crack propagation). However, without an experimentally well-defined R-curve for this material, it is not appropriate to provide any other estimates than the simplified one presented here.
Figure 3.18: Load-crack extension curve for alloy B based on in-situ CNB test measurements (Fig. 3.16) were used to estimate the fracture toughness of a fully eutectic alloy D specimen (Fig. 3.13b) in which the disilicide reinforcements within the eutectic colonies are oriented perpendicular to the crack propagation direction. The data point marked by the black square is the load and crack extension at which the crack was observed to leave the notch plane in Fig. 3.13b. The load-crack extension data was fitted using a linear function in the regime governed solely by the material’s R-curve behavior (i.e. where the stress intensity function for the chevron-notch geometry produces an increasing elastic strain energy release rate, or more simply, unstable fracture).

3.4 Discussion

3.4.1 Considerations of alloy and process design on the isotropy of the fracture toughness of in-situ toughened Si-(Cr,V)Si_2 alloys processed using multidirectional solidification

Most of the development of in-situ composites based on ceramic systems has primarily focused on directionally solidified eutectics, where advantage of the composite’s mechanical anisotropy is taken by ensuring that fracture of the material occurs perpendicular to the reinforcements (i.e. by loading the material along the reinforcement direction). However, for multidirectional solidified alloys, where isotropic fracture properties are desired, it is pertinent to obtain a
homogenous microstructure with a broad distribution of reinforcement orientations. During normal eutectic solidification, coupled growth of the phases leads to spatial regularity and a preferred orientation of the phases – the latter of which is controlled primarily by the processing conditions. In contrast, anomalous eutectic solidification can lead to independent or loosely coupled growth of the phases, resulting in a much more randomly oriented microstructure. In this case, the orientation of the phases can be controlled by both processing conditions and alloy composition (via the eutectic morphology). Therefore, both alloy and process design must be considered in the development of in-situ Si-(Cr,V)Si$_2$ produced through multidirectional solidification techniques.

In Section 3.3, it was shown that the morphology of Si-(Cr,V)Si$_2$ alloys can be manipulated (Figs. 3.5 - 3.8) through the volume fraction of the minor disilicide phase [(Cr,V)Si$_2$] by varying the alloy composition (Table 3.3). More specifically, it was found that as the volume fraction of (Cr,V)Si$_2$ was increased, the morphology changes from a fibrous (alloy A, $V_f = 6.7 \%$) to a massive branched (alloys B, $V_f = 19.9 \%$) to a massive branched/complex regular (alloy C, $V_f = 23.8 \%$) to a quasi-regular colony type structure (alloy D, $V_f = 39.6 \%$) – each containing a higher degree of disilicide alignment than its predecessor. As a result of this morphological transition, the fracture properties of alloys with higher (Cr,V)Si$_2$ volume fractions tended to be more dependent on the orientation of the disilicide reinforcements. The clearest example of this type of anisotropy was found in alloy D. For alloy D specimens machined from the sides of the casting, a dependence of the measured fracture toughness on the notch orientation (Table 3.4) was linked to the disilicide growth orientation with respect to the crack (notch) plane (Fig. 3.9). For alloy D specimens machined from the center of the casting, eutectic colonies that were aligned parallel to the cracking direction during CNB testing (Fig. 3.13a and 3.17) provided low fracture resistance paths through which cracks can easily propagate with minimal deviation in its path. On the other hand, eutectic colonies oriented perpendicular to the crack path (Fig. 3.13b) provided a high resistance to fracture through deflection and bridging mechanisms. It is thus obvious that for anomalous eutectic alloys, such as Si-(Cr,V)Si$_2$, increasing the volume fraction of the reinforcing minor phase (thereby promoting more well-aligned microstructures) can potentially induce unwanted anisotropy in castable in-situ composites designed for non-directional processing methods.
Based on the above discussion, it can be inferred that one way to achieve a broad distribution of reinforcement orientations is by actually reducing the volume fraction of the minor phase to promote a more irregular structure such as those exhibited by alloys B and C. Both of these alloys exhibited a branched type structure in which the reinforcements naturally cover a broader distribution of orientations compared to the well-aligned quasi-regular structure exhibited by alloy D. This is perhaps most clearly observed in the micrographs taken during the in-situ CNB testing of alloy B (Fig. 3.16) for which a high degree of crack bridging is observed during crack extension. Alloy B also displayed the maximum toughness measured by both the Instron (Table 3.4) and in-situ (Table 3.6) CNB test methods, which suggests an advantage of the irregular massive branched structure in attaining isotropic fracture properties. Of course, this method of achieving isotropic fracture properties is contradictory to conventional composite design techniques (Section 1.4) which normally seek to maximize the volume fraction of reinforcements in the composite microstructure. In order to take advantage of the high volume fraction of disilicide reinforcements produced through Si-CrSi$_2$ eutectic solidification, without inducing mechanical anisotropy, the processing method must be refined. For example, nucleation agents can be used so that the eutectic grains do not preferentially grow from the mold walls. Instead, the grains will nucleate homogenously during solidification, resulting in a microstructure composed of randomly oriented eutectic colonies (schematically depicted in Fig 3.19). As a crack moves through a region of low crack resistance (marked in green), it is likely that it will encounter regions of high crack resistance (marked in red) that force the crack to either deflect out of its plane and/or become bridged by reinforcements before reaching another low energy fracture path. This, in effect, minimizes the extent of crack growth that occurs before the toughening mechanisms of the composite are activated, allowing significant R-curve behavior to be realized.
Figure 3.19: Schematic of a eutectic colony microstructure which exhibits a random distribution of the reinforcing minor phase orientation as marked by the bold lines or circles (circles represent an orientation into the plane of the page). As a crack propagates through a region low crack resistance region (where the colony is oriented parallel to the crack direction), it is likely to encounter regions of high crack resistance (where the colonies are oriented more perpendicular to the crack direction) before finding another low crack resistance path. This type of microstructure is expected to enhance the isotropy of in-situ toughened Si-(Cr,V)Si$_2$ alloys by ensuring that microstructural toughening mechanisms, such as crack bridging, are activated prior to excessive crack growth.

3.4.2 Effect of overgrowth during anomalous eutectic solidification on the observed long-crack fracture toughness of in-situ toughened Si-(Cr,V)Si$_2$ alloys

In addition to their dependence on alloy composition, anomalous eutectic structures are also strongly affected by their growth velocity. During rapid solidification of Si-(Cr,V)Si$_2$ alloys, overgrowth of the non-faceted silicon phase is enhanced, especially for off-eutectic compositions where silicon is the primary phase. As discussed in Section 3.3, these overgrown Si regions act as low energy fracture paths that severely degrade the overall toughness displayed by the composites (Figs. 3.14 and 3.15d-f). Increasing the volume fraction of the (Cr,V)Si$_2$ phase helps to restrict overgrowth of the silicon phase, thereby reducing the tendency of Si regions to form and improving the mechanical reliability of Si-(Cr,V)$_2$ composites. This is demonstrated by the increase in average fracture toughness with increased disilicide content (Table 3.4). Reduction
of overgrowth can also be achieved by decreasing the growth velocity, as exemplified by the microstructures of alloy D specimens machined from the sides (Fig. 3.9) and center of the casting (Fig. 3.8), where the solidification rate decreases from the former to the latter. However, in this case, overgrowth is also affected by the segregation of solute to the central region of the casting during solidification causing the alloy to approach its eutectic composition. It is also important to note that reducing the growth velocity has the negative effect of increasing the eutectic spacing.

Figure 3.20 illustrates how the presence of overgrown Si regions can affect the long-crack fracture toughness achieved by Si-(Cr,V)Si2 composites during CNB testing. Schematic R-curves (K_R) for two alloys of the same composition are shown, where alloy X1 is free of overgrown Si regions and alloy X2 contains large Si regions near the crack initiation site (note that the slopes of the R-curves are exactly the same for both alloys). Due to the presence of large Si regions in alloy X2, the rising R-curve behavior is delayed until larger crack extensions compared to alloy X1. Thus, the stress (or load) required to extend the crack to the minimum stress intensity point (marked as an open circles at Δa = 0.10) is smaller for alloy X2 than for alloy X1. At the minimum stress intensity, alloy X1 has already reached a toughness value towards the upper region of the R-curve and can only sustain small additional increases in the applied stress (Δσ') until unstable fracture occurs at K_I(Δa) ≈ 4. For alloy X2, the apparent toughness is towards the lower region of the R-curve at the point where the minimum stress intensity factor is reached. Since the R-curve is still steeply rising, the alloy can sustain greater additions in the applied stress (Δσ") after reaching the minimum stress intensity. However, the maximum attained toughness (at K_I(Δa) ≈ 3) is still not as high as that observed for the first alloy whose R-curve behavior was activated at earlier crack extensions. The example presented here is meant to explain the differences in long-crack toughness as measured by the CNB experiments in this study. The variability of fracture toughness due to Si overgrowth is expected to be even more severe for naturally occurring flaws where the stress intensity increases much more rapidly than for the experimental notch configuration.
Figure 3.20: Illustration showing how postponement of the rising R-curve behavior in Si-(Cr,V)Si₂ alloys leads to reduced fracture toughness values ($K_{Ivb}$) as measured by the CNB method. In this example, the delayed rising R-curve response of alloy X₂ compared to an alloy X₁ of the same composition is due to the presence of overgrown silicon regions near the notch tip which provide low energy fracture paths. This type of effect is expected to greatly reduce the reliability of Si-(Cr,V)Si₂ composites.

3.5 Concluding Remarks

Analysis of the long-crack behavior of die cast, in-situ toughened Si-(Cr,V)Si₂ composites revealed that these materials display the crack deflection and bridging toughening mechanisms that were predicted during the alloy design stage (Section 1.4). Fracture toughness values between 2-3 times that of unalloyed silicon ($K_{IC} = 0.8 – 1.0$ MPa·m$^{1/2}$) were measured for the composites, with many of the alloys either approaching or exceeding that displayed by commercial Hexoloy® SA SiC (2.88 ± 0.04 MPa·m$^{1/2}$). However, the microstructural-mechanical property relationships for these composites are complicated by the strong dependency of anomalous eutectic growth on both alloy composition and processing conditions. Increases in the (Cr,V)Si₂ reinforcement volume fraction (with increasing Cr alloy additions) tends to increase the average fracture toughness exhibited by the alloys, as expected from conventional composite design theory. At the same time, however, increasing the minor (Cr,V)Si₂ phase volume fraction inherently leads to a higher degree of alignment of the
reinforcements and thus anisotropy of the fracture properties (which may be undesirable for multi-directional solidified alloys). A reduction of the (Cr,V)Si$_2$ volume fraction to achieve a more irregular eutectic morphology (with a broader distribution of disilicide orientations) helps to improve the isotropy in fracture toughness, but leaves the alloy more susceptible to overgrowth of the silicon phase – particularly when it solidifies as the primary phase. Thus, in addition to tailoring the alloy composition, refinements in the processing technique must also be made in order to fully optimize the Si-(Cr,V)Si$_2$ composite microstructure for maximum toughness. For example, nucleation agents can be used to ensure homogenous nucleation of eutectic grains during solidification, thereby resulting in a random distribution of colony orientations (for complex regular or quasi-regular growth). By refining the solidification process in this way, it is envisioned that the advantages of increased disilicide (reinforcement) content on fracture toughness can be taken without sacrificing its mechanical isotropy.
Chapter 4: Effects of microstructural toughening on the sliding wear resistance of in-situ toughened Si-(Cr,V)Si₂ alloys

4.1 Role of microstructural toughening on wear response of Si-(Cr,V)Si₂ alloys

Increasingly popular use of engineering ceramics as tribological components has motivated the need to develop predictive models [153-156] of the wear behavior for these materials. The suitability of a given model is based on the dominant wear mechanism under a given set of operating conditions. Each model can depend on the material’s microstructure and mechanical properties in a quite complex manner – especially for those materials that display rising R-curve behavior. For example, studies of silicon nitride (Si₃N₄) ceramics [157, 158] with heterogeneous microstructures (i.e. mixture of equiaxed and elongated grains), have shown that the short-crack, rather than the long-crack, toughness is the pertinent material property governing the wear resistance during abrasive wear. In other cases, studies have found that microstructural features that lend themselves to improved long-crack toughness, are actually detrimental to the material’s wear resistance which is dominated by short-crack events. In alumina (Al₂O₃), for example, internal stresses in the composite matrix (from thermal expansion mismatch between grains), are responsible for the crack-bridging toughening mechanism induced by grain interlocking. However, during the wear process, these internal stresses lead to multiple microcracks at the grain boundaries which can coalesce and result in severe grain boundary cracking and grain pull-out [159-161]. The same type of paradoxical relationship has been observed between the long-crack toughness and wear resistance of ceramics reinforced with whiskers or second (transformation toughening) phases [162]. That is, the microstructural features (such as weak interfaces and internal stresses) intentionally designed to improve long-crack fracture resistance actually degrade the short-crack response of the materials during wear.

In Chapter 3, it was shown that the long-crack fracture toughness of silicon could be improved by the incorporation of (Cr,V)Si₂ disilicide reinforcements (via eutectic solidification) to form Si-(Cr,V)Si₂ composites. Weak interfaces between the silicon and disilicide phases lead to crack deflection and bridging during crack propagation, and as a result, an increase in apparent toughness with increasing crack extension (i.e. a rising R-curve). Based on the above discussion,
it is of high practical interest to explore whether or not the microstructural toughening mechanisms observed during the long-crack response of Si-(Cr,V)Si$_2$ alloys imparts a similar improvement in the short-crack response of these materials during wear. This topic is the focus of the present chapter.

### 4.2 Experimental Procedures

#### 4.2.1 Alloy preparation

Four Si-(Cr,V)Si$_2$ alloys (Table 4.1), as well as an unalloyed silicon sample, were prepared by induction melting the appropriate ratios of starting materials (99.98 % Si chunks, 99.7 % V granules, 99.995 % Cr pieces) using an Inductotherm Dura-Line® furnace. Alloys were melted inside of graphite crucibles (10.16 cm OD x 6.35 cm ID x 12.70 cm deep (15.24 cm high), GR008G**) and poured into 0.0015 m$^3$ graphite molds (GM-111**) in air. The dimensions of the graphite molds are listed in Table 4.2. Prior to melting the alloys, the graphite crucible and mold were baked in air at 500 °C for 2 hours to drive off moisture. Induction melting was performed using power settings of 70kW, 800 V, and 2300 Hz. The total time needed for complete melting of the alloy was approximately 5 - 10 min.

#### Table 4.1: Alloy compositions used for sliding wear analysis

<table>
<thead>
<tr>
<th>Alloy Designation</th>
<th>Alloy Composition (wt. %)</th>
<th>$V_f^{MSi_2}$ (%)$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>100.00</td>
<td>0.00</td>
</tr>
<tr>
<td>E</td>
<td>91.20</td>
<td>2.33</td>
</tr>
<tr>
<td>F</td>
<td>86.18</td>
<td>11.27</td>
</tr>
<tr>
<td>G</td>
<td>81.40</td>
<td>17.60</td>
</tr>
<tr>
<td>H</td>
<td>78.33</td>
<td>21.67</td>
</tr>
</tbody>
</table>

$^*$ $V_f^{MSi_2}$ values are those theoretically predicted from the phase fraction calculations in Section 2.4.1 (Table 2.2).

**GR008G and GM-111 refer to the grades of graphite used for the crucibles and molds, respectively. The GR030 is a superfine grain, high density extruded graphite rod and GM-111is a very fine-grained, isostatically pressed graphite (further material properties can be found on the supplier’s site at https://www.graphitestore.com).
Table 4.2: Dimensions of graphite molds used to cast alloys for wear experiments

<table>
<thead>
<tr>
<th>Outer Length (cm)</th>
<th>Inner Length (cm)</th>
<th>Outer Width (cm)</th>
<th>Inner Width (cm)</th>
<th>Height (cm)</th>
<th>Depth (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.62</td>
<td>5.03</td>
<td>6.99</td>
<td>4.70</td>
<td>3.18</td>
<td>1.59</td>
</tr>
</tbody>
</table>

4.2.2 Wear Testing

After alloy preparation, flat 1" by 1" plate wear specimens (0.25" thick) were precision cut (Ferro-Ceramic Grinding, Inc. Wakefield, MA) from the castings. Wear tests were carried out with a CSM Instruments® ball-on-disk tribometer (Fig. 4.1). Test specimens were mechanically fixed to the sample stage and rotated beneath a tungsten carbide (WC) ball (having a hardness of 22 GPa and a radius of 6mm) at a linear sliding velocity of 0.15 m/s under normal loads (W) ranging from 1 - 6 N (note: test at loads of 2N were only performed for Si). The radius of rotation for the tests was 8 mm. Each test was performed for 10,000 cycles in an ambient atmosphere at room temperature (25 ± 2°C). The entire test fixture was isolated within an attached enclosure in order to ensure a constant test environment and to reduce any effects of external noise on the friction coefficient (μ) measurements taken during the experiments. Each sample was cleaned in acetone prior to testing, and no lubrication was used during the tests.

Figure 4.1: Ball-on-disk test apparatus used for wear testing of Si and Si-(Cr,V)Si₂ composites. (Image reproduced from http://www.csm-instruments.com/en/Tribometer)
The normalized volume of material removed during the wear test was determined by performing a 3-D profilometry scan of the resulting wear track using a Tencor® P-16 surface profilometer with a 2 µm radius diamond stylus. A stylus force of 2 mg was used for each scan. The sample was aligned such that there was negligible curvature of the track in the area of interest (i.e. the scanned area of the wear track was rectangular). The scan area was 1000 x 300 µm, which included a total of 11 linear scans per measurement. Apex® 3D software was then used to generate a mean profile for the data. The normalized wear volume was determined by integrating the area \( A \) under the wear profile (as well as any pile-up areas on the sides of the wear track) using MATLAB® software. The normalized wear volume \( V \) was calculated as:

\[
V = \frac{v}{x} = \frac{2\pi r \cdot A}{2\pi r \cdot 10,000 \text{cycles}} = \frac{A}{10,000}
\]  

(4.1)

where \( v \) is the total wear volume, \( x \) is the sliding distance, and \( 2\pi r \) is the circumference of the wear track. Thus, the normalized volume is simply the area under the wear profile divided by 10,000 laps and has units of area (m²). For each specimen, this procedure was performed in four regions of the wear track (one measurement per quadrant) to obtain an overall average of the wear volume.

4.2.3. Hardness Testing

Vickers hardness measurements were made on metallographically prepared specimens of as-received Si, as well as on arc-melted buttons of CrSi₂ (99+ %) and VSi₂ (99.5 %) powders (see Section 2.2.1 for more details on the arc melting process). Measurements were taken using a LECO LM-247AT microhardness tester with the ConfiDent® testing program and Pax-It® imaging software. Each measurement was performed using a load of 10 g and a dwell time of 15 s. Based on these measurements, the total hardness of the composites \( H^{\text{composite}} \) was calculated using a rule of mixtures:

\[
H^{\text{composite}} = V_f^{\text{Si}} \cdot H^{\text{Si}} + V_f^{\text{MSi}_2} \cdot H^{\text{MSi}_2}
\]  

(4.2)
where \( V^\text{Si}_f, V^\text{MSi}_f \) and \( H^\text{Si}, H^\text{MSi} \) are the respective measured volume fractions and Vickers hardness of the silicon and disilicide phases present in the alloys. Volume fraction measurements were taken using the EDS segmentation procedure described in Section 3.3.1. For alloys with the mixed \((\text{Cr}, \text{V})\text{Si}_2\) disilicide phase, a weighted average (based on the relative compositional percentages of Cr and V) was used to calculate the hardness of this phase. Alloy E \([\text{Si-1.32Cr-2.75V (at. %)}]\), for example, has a relative atomic fraction of 0.32 Cr \([= 1.32 / (2.75 + 1.32)]\) and 0.68 V \([= 2.75 / (2.75 + 1.32)]\). Thus, the hardness of the disilicide phase for this alloy would be taken as: \((0.32 \cdot H^{\text{CrSi}_2}) + (0.68 \cdot H^{\text{VSi}_2})\).

4.3 Experimental Results

4.3.1 Microstructural analysis

A light optical micrograph of the as-cast unalloyed silicon (Fig. 4.2a) shows an extremely coarse structure with grains reaching sizes of up to several hundred microns to millimeters. Twin boundaries traversing across grains were also commonly observed in the silicon microstructure. Scanning electron micrographs of the Si-(Cr,V)Si\(_2\) alloys show that the microstructures resemble those observed for the alloys studied during the fracture experiments (Chapter 3). Ternary alloys E (Fig. 4.2b), F (Fig. 4.2c), and G (Fig. 4.2d) display a mixture of an irregular and complex regular structure, just as was seen for alloy C (Fig. 3.7). Compared to the ternary alloys B (Fig. 3.6) and C (Fig. 3.7) from the fracture studies, the degree of silicon overgrowth was found to be much larger in alloys E-G. This is in alignment with the predictions that alloys B and C lie slightly to the left of the eutectic boundary curve, while alloys E-G lie further to the right of the eutectic curve (Fig. 2.13) where primary Si solidification, and thus excessive Si overgrowth, is expected to take place. Binary alloy H (Fig. 4.2e,f) displays a colony type structure similar to that of binary alloy D (Figs 3.8 and 3.9). As noted in Chapter 3, the increase in volume fraction of the disilicide phase (from alloy E-H), induces a higher degree of alignment of the reinforcements in the composite alloy. Measured volume fractions of the disilicide phase (Table 4.3) were again found to be slightly lower (~1-7 %) than the calculated values, primarily due to the effects of solute segregation during non-equilibrium solidification (Table 4.3).
Figure 4.2: (a) As-cast unalloyed silicon displays a coarse microstructure consisting of large ($10^2$-$10^3 \mu m$) grains. Ternary (b) alloy E ($V_f = 14.9 \%$), (c) alloy F ($V_f = 20.8 \%$), and (d) alloy G ($V_f = 27.4 \%$) display a mixed irregular and complex regular structure. Binary (e) alloy H [magnified in (f)] displays a colony structure. (Silicon etched with 200 mL distilled H$_2$O and 100 g NaOH. SEM images taken using secondary imaging at an accelerating voltage of 20 kV)
Table 4.3: Experimental versus calculated disilicide volume fractions

<table>
<thead>
<tr>
<th>Alloy Composition (wt %)</th>
<th>% (Cr,V)Si₂ (exp.)</th>
<th>% (Cr,V)Si₂ (calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-2.33Cr-4.74V (Alloy E)</td>
<td>14.89 ± 0.6</td>
<td>15.2</td>
</tr>
<tr>
<td>Si-11.27Cr-2.55V (Alloy F)</td>
<td>20.81 ± 3.3</td>
<td>24.4</td>
</tr>
<tr>
<td>Si-17.60Cr-1.00V (Alloy G)</td>
<td>27.37 ± 2.9</td>
<td>33.6</td>
</tr>
<tr>
<td>Si-21.67Cr (Alloy H)</td>
<td>31.74 ± 2.1</td>
<td>39.5</td>
</tr>
</tbody>
</table>

4.3.2 Wear tests

Examples of wear track profiles measured for silicon and alloy H at loads of 1, 3, and 6 N (Fig. 4.3) demonstrate the transition in the material removal rate (i.e. wear mechanism) with increasing load for the unalloyed and alloyed materials. At low loads (W = 1 N), very little material removal is observed to occur in either Si (Fig. 4.3a) or alloy H (Fig. 4.3b) and the track topologies are irregular and jagged. In fact, for alloy H, most of the wear volume is from pile-up, or displacement, of material to the sides of the wear track. These types of responses are indicative of mild wear, in which the dominant mechanism of material removal is adhesion or microfracture caused by sub-critical stress intensities at asperity tips [163]. As the load is increased to 3 N, severe wear begins to occur in unalloyed Si and a well-developed, deep (~ 12 μm) wear track is found underneath the specimen surface (Fig. 4.3c). Such gross wear is indicative of macroscopic fracture events caused by contact stresses that exceed the fracture toughness (Klc) of the material [164]. This leads to an increased number of third-body wear particles (such as dislodged grains) and hence an accelerated rate of wear. The transition into the severe wear regime is delayed in the composite material, as noted by the extremely shallow depth of wear observed for alloy H (Fig. 4.3d) – about ten times less than that measured for Si at the same 3 N load. As will be discussed in Section 4.4.1, the delay in the mild-to-severe wear transition can be attributed to the improved toughness of the Si(Cr,V)Si₂ composites (Chapter 3). At a load of 6 N, fully developed wear tracks (i.e. severe wear) are observed for both materials.
Figure 4.3: Wear track profiles measured for unalloyed Si and alloy H after testing at three different normal loads. At 1 N, both (a) silicon and (b) alloy H display very mild wear indicative of a microfracture wear mechanism. At 3 N, (c) silicon starts to undergo severe wear caused by macrofracture events, whereas (d) alloy H still displays a low wear rate due to enhanced toughening in the composite. At 6 N, both (e) Si and (f) alloy H undergo severe wear.
However, the total volume of material removed for alloy H is about 3 times less than that of silicon.

Additional insights as to the shift in deformation mechanism with increasing load were given by the friction coefficient measurements. At a load of 1 N, all of the materials displayed the same trend of a decrease in $\mu$ during the initial run-in state (around the first 2,000 laps), followed by a smooth increase in the coefficient to a range of 0.7 – 0.9 (Fig. 4.4a). This range of friction coefficients is relatively high, indicating that adhesive modes of wear were likely existent under these testing conditions. This agrees with the observation that both unalloyed silicon and alloy H (which was typical of all the Si-(Cr,V)Si$_2$ alloys) underwent mild wear at this load (Fig. 4.3a,b).

At a load of 3 N, a much noisier $\mu$-curve is measured for the unalloyed Si specimen, while all of the Si-(Cr,V)Si$_2$ alloys retain a relatively smooth $\mu$-curve up to their steady-state value ranging from 0.55-0.70 (Fig. 4.4b). The undulating shape of the Si $\mu$-curve at this load is reasoned to be due to the dynamic fracturing and removal of wear debris from the surface of the test specimen; the peaks corresponding to the fracture events and the valleys to (easy) material removal. Again, this agrees with the conclusions drawn from the wear track profiles that silicon transitions into the severe wear regime at a load lower than that of the Si-(Cr,V)Si$_2$ alloys due to its lower fracture resistance. At a load of 6 N, the aforementioned undulating frictional behavior is seen for silicon, as well as for alloys E and F. On the other hand, alloys G and H still display relatively smooth $\mu$-curves, suggesting that large-scale material removal is minimal during these tests. As will be discussed in Section 4.4.1, the difference in wear behavior (just as with long-crack behavior) is partially related to the dependence of fracture toughness on microstructural features such as increased volume fractions of disilicide reinforcements (Table 4.3) and less observed Si overgrowth of alloys G and H compared to alloys E and F (Figure 4.2). Of course, improved wear properties can also be attributed to increased hardness of the composite alloys. In Section 4.4.1, an attempt is made to distinguish between the effects of improved hardness and fracture toughness through application of an appropriate fracture-based wear model which takes both of these properties into account.
Figure 4.4: The shapes of the coefficient of friction (μ) curves during sliding wear can be identified with an underlying mode of wear for the given testing conditions. (a) At W = 1 N, very smooth curves and high values of μ indicate that adhesive wear mechanisms (characteristic of mild wear) are active at low loads. (b) At W = 3 N, the Si-(Cr,V)Si₂ alloys display the same smooth curves as in (a) indicating they are still within the mild wear regime. However, the ‘noisy’, undulating curve displayed for Si at this load indicates successive fracturing (peaks) / material removal (valleys) events are taking place. (c) At W = 6N, silicon and two of the composite alloys (alloy E and F) are shown to display undulating μ-curves, whereas alloys G and H maintain smooth curves suggesting that large-scale material removal is minimal for the latter two alloys.
In order to appreciate the wear performance of the alloys and compare their wear resistance to other engineering materials, it is convenient to use a form of Archard’s law which broadly describes wear rates at sliding velocities less than 1 m/s:

\[ \frac{K}{H} = \frac{v}{xW} \left( = \frac{V}{W} = \frac{A}{10,000 \cdot W} \right) \]

(4.3)

where \( K \) is the probability of wear particle formation during asperity contact, \( H \) is the hardness of the material being tested, and \( W \) is the applied load. The right hand term was calculated using the expression for the normalized wear volume given in Eq. 4.1 and is a quantity commonly referred to as the specific wear rate or the wear rate constant \( (k_a) \) and is inversely proportional to wear resistance. Figure 4.5 plots the wear rate \((m^2/N)\) constant measured for the five test specimens as a function of the applied load. For loads over 1 N, where large-scale fracture mechanisms are activated during sliding wear (Fig. 4.3), the specific wear rate of Si \(( \approx 10^{-13} \text{ m}^2/\text{N})\) was found to be about an order of magnitude higher than that of the alloys \(( \approx 10^{-14} \text{ m}^2/\text{N})\).

The magnitude of the wear rate constants found for the composites are typical of those displayed by engineering ceramics, cermets, and nitrided steels – all of which are known to be optimal materials for wear situations, especially when abrasive wear is of most concern [166].
Figure 4.5: Comparison of the wear rate constant (right-hand term of Eq. 4.3) for Si and the Si-(Cr,V)Si$_2$ alloys within fracture-dominated wear regimes ($W \geq 2$ N) show that the alloys display wear rate constants (which are inversely proportional to wear resistance) an order of magnitude lower than unalloyed Si. The region highlighted in blue signifies the typical range of wear rate constants displayed by technical engineering ceramics commonly used as tribological components.

4.3.3 Hardness Measurements

Vickers hardness ($H_V$) measurements for the as-received Si and the arc-melted CrSi$_2$ and VSi$_2$ samples are listed in Table 4.4, along with the calculated composite hardness values using Eq. 4.2. The hardness measured for silicon falls within the range of values measured for this material; for example, the value of 8.7 GPa has been reported for $p^+$-type single crystalline silicon tested by nanoindentation [134]. The hardness measured for CrSi$_2$ and VSi$_2$ are in very close agreement with those reported by Goldschmidt [80] ($H_V^{CrSi_2} = 11.07$ GPa, $H_V^{VSi_2} = 10.68$ GPa) and by Shishido et al. [167] for single crystalline CrSi$_2$ ($H_V^{CrSi_2} = 11.2 \pm 0.4$ GPa).
Table 4.4: Vickers hardness for Si, CrSi$_2$, VSi$_2$ and Si-(Cr,V)Si$_2$ alloys

<table>
<thead>
<tr>
<th>Specimen</th>
<th>HV (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-received (unalloyed) Si</td>
<td>8.8 ± 0.5</td>
</tr>
<tr>
<td>CrSi$_2$</td>
<td>11.0 ± 1.0</td>
</tr>
<tr>
<td>VSi$_2$</td>
<td>10.5 ± 0.9</td>
</tr>
<tr>
<td>Alloy E</td>
<td>9.1 ± 0.6</td>
</tr>
<tr>
<td>Alloy F</td>
<td>9.2 ± 0.6</td>
</tr>
<tr>
<td>Alloy G</td>
<td>9.4 ± 0.6</td>
</tr>
<tr>
<td>Alloy H</td>
<td>9.5 ± 0.7</td>
</tr>
</tbody>
</table>

* Hardness values listed for alloys E-H are calculated based on Eq. 4.2.

4.4 Discussion

4.4.1 Effects of microstructural toughening on the wear response of Si-(Cr,V)Si$_2$ alloys during sliding wear

In Section 4.3.2, it was shown that Si-(Cr,V)Si$_2$ alloys display improved wear properties compared to the unalloyed Si matrix under severe wear conditions dominated by fracture-based deformation mechanisms. To provide a physical basis for the observed behaviors, the Evans and Marshall [153] lateral fracture model (Eq. 4.4) was used to correlate the measured wear volumes with the mechanical properties (more specifically, the hardness and fracture toughness) of the tested materials:

$$
V = \frac{\alpha_3}{K_c^{1/2}} \cdot \frac{W^{9/8}}{H^{5/8}} \left( \frac{E}{H} \right)^{4/5}
$$

(4.4)

where the $V$ is the normalized wear rate (Eq. 4.1), $W$ is the applied load (N), $H$ is the sample hardness (GPa), $K_c$ is the fracture toughness (MPa·m$^{1/2}$), $E$ is the Young’s modulus (GPa), and $\alpha_3$ is a material-independent constant that depends on the asperity geometry. This model is widely
used to describe the temperature-independent abrasive wear rate of a brittle material under dry sliding conditions. As the name suggests, the model is based on the underlying fracture mechanics of the lateral crack system [168] that is formed underneath a sharp indenter. In the case of sliding wear, the ‘sharp indenters’ can be the actual counterbody against which the test specimen is sliding or they can be second-, third-body asperities (such as wear debris, dislodged grains, etc.) sliding against the specimen surface. Figure 4.6 (adapted from [169]) illustrates the crack system formed underneath a sharp asperity during sliding wear. The highlighted regions show the potential chipping zones from which material can be removed due to the propagation of lateral cracks (in a direction perpendicular to the sliding direction) to the surface of the material.

![Potential chipping zone](image)

**Figure 4.6:** Illustration depicting the crack system formed underneath a sharp asperity during sliding wear. Lateral cracks that form underneath the surface and propagate perpendicular to the sliding direction can reach the surface of the material, causing extensive material removal (highlighted in red). (Image was adapted from [169])

In Fig. 4.7, the normalized wear rates (converted to mm$^3$/m) measured for Si and the Si-(Cr,V)Si$_2$ alloys are plotted against the applied load. An obvious change in the mode of wear is indicated in this dataset by a drastic increase in the slope of the data, or in other words, a more rapid increase in the wear rate with applied load. This transition corresponds to the change from mild (i.e. adhesive, microfracture) to severe (i.e. lateral fracture) wear as described in Section
4.3.2. For unalloyed Si, the critical load required to induce severe wear ($W_{c}^{\text{Si}}$) is shown to be 1 N, while the critical load for the alloys ($W_{c}^{\text{alloys}}$) is around 4 N. It is beyond this critical load that the lateral fracture model [153] is applicable to describing the wear behavior.

![Figure 4.7: Plot of the wear rate versus applied load during sliding wear of Si and Si-(Cr,V)Si$_2$ alloys shows a transition from mild to severe wear as indicated by an increase in the slope of the data. The critical load necessary to induce this transition was found to be lower for Si ($W_{c} = 1$ N) than for the alloys ($W_{c} = 4$ N).](image)

Using only the data corresponding to severe wear in Fig. 4.7 (i.e. $W > W_{c}$), the wear rates were plotted against the second mechanical property factor term on the right hand-side of Eq. 4.4 using the units listed in parenthesis for each term given after the equation (Fig. 4.8). The Young’s modulus for the composites was calculated in the same manner as the hardness (Eq. 4.2) by using the Young’s moduli for Si, CrSi$_2$, and VSi$_2$ listed in Table 1.6 ($E_{\text{Si}} = 150$ GPa, $E_{\text{CrSi}_2} = 347$ GPa, and $E_{\text{VSi}_2} = 331$ GPa). The linear scaling between the wear rates and the mechanical property factor (given by the slope of $\alpha_{3}/K_{c}^{1/2}$) for silicon, as well as its extrapolation to the origin, is an encouraging indication that the lateral fracture model accurately characterizes the active wear mechanism for this material under the given set of testing conditions. However,
the lines of best fit for the alloy wear data do not pass through the origin, indicating that the 
model misses some facet of the wear behavior of the alloys for the same set of testing conditions. 
As will be discussed in Section 4.4.2, this inconsistency is due to the crack-size dependence of 
the composite toughness as a result of their rising R-curve behavior.

![Graph showing linear correlation between wear rates and mechanical property factors.](image)

**Figure 4.8:** Linear correlation between the wear rates and mechanical property factors (from Eq. 4.4) for Si and Si-(Cr,V)Si₂ alloys indicates the lateral fracture model is appropriate for describing the material removal process within the severe wear regime for the given set of testing conditions.

Microscopic analysis of the wear tracks after testing at large loads (e.g. W = 6 N) clearly revealed the effects of microstructural variation on the wear behavior of the different materials (Fig. 4.9). After testing unalloyed Si, very large wear debris composed of Si grains were found on the sides of deep grooves formed by the plowing action of asperities along the specimen surface (Fig. 4.9a). This illustrates the ease with which lateral cracks can propagate to the surface of this material during the wear process. In alloy F, evidence of crack bridging is observed to prohibit such pullout of large grains from the primary (or overgrown) Si regions.
(Fig. 4.9b). Microfracture within the large Si regions was also found to have contributed to the overall wear volume in alloy F (as well as in the other ternary Si-(Cr,V)Si$_2$ alloys E and G). In alloy H, no large wear debris are observed to have formed due to the absence of overgrown Si regions in this alloy. Instead, small wear particles are found to have been removed and compacted into a thin tribolayer on the wear surface (Fig. 4.9c). It is interesting to note that the eutectic colonies of alloy H are all oriented perpendicularly to both the sliding direction and lateral crack plane (schematically shown in Fig. 4.9d). This orientation relationship between the disilicide reinforcements and lateral crack plane is likely to have resulted in a relatively high apparent fracture toughness during wear.
Figure 4.9: SEM analysis of the wear tracks of test specimens taken after testing at a load of 6 N reveal the effects of microstructural toughening on the wear response of these materials. (a) Deep asperity grooves and large wear debris show ease of lateral crack propagation in Si. (b) Crack bridging within the eutectic regions of alloy F is shown to prevent large Si fragments from becoming removed from the specimen surface. (c) No large wear fragments are shown to have formed in alloy H due to the lack of overgrown Si regions. Instead, a thin tribolayer consisting of small, compacted wear particles is present on the surface of the specimen. (d) Illustration showing the orientation relationship between the sliding direction, lateral crack planes, and eutectic colonies of alloy H shown in (c). (SEM images taken using (a) secondary and (b), (c) back-scattered imaging at an accelerating voltage of 20 kV)
4.4.2 Lateral fracture model with R-curve effects

The inability of the lateral fracture model to capture the microstructural aspects associated with fracture-based wear, such as a rising R-curve, can be seen by the fact that the extrapolations of the best fit lines to the wear data for the Si-(Cr,V)Si₂ alloys do not pass through the origin, as they do for unalloyed Si, which displays a flat R-curve (Fig. 4.8). The source of the discrepancy is embedded within the lateral crack length \( a \) equations \[153\]:

\[
a = a^L \left[ 1 - \left( \frac{W_c}{W} \right)^{1/4} \right]^{1/2}
\]

(4.5a)

\[
a^L = \alpha_1 \left( \frac{E/H}{K_c^{1/2} H^{1/8}} \right)^{5/8} W^{5/8}
\]

(4.5b)

where \( a^L \) is known as the limiting crack function \[168\] and \( \alpha_1 \) is a material-independent constant (similar to that of \( \alpha_3 \) in Eq. 4.4). This limiting crack function is directly linked to the \( V \propto 1/K_c^{1/2} \) proportionality in Eq. 4.4. When the particle contact load is much greater than the critical load to nucleate lateral cracks (i.e. \( W >> W_c \)), \( a \approx a^L \). This critical load, however, is highly dependent on the fracture toughness of the material as given by the apparent threshold equation \[153\]:

\[
W_c = \zeta \left( \frac{K_c^4}{H^3} \right) f(E/H) \approx (2 \cdot 10^5) \left( \frac{K_c^4}{H^3} \right)
\]

(4.6)

with \( f \) being a slowly varying function of \( E/H \) such that \( \zeta f(E/H) \approx 2 \cdot 10^5 \). For rising R-curve materials, the toughness increases with crack size; the crack size increases with load. Thus, the critical load can actually rapidly increase \( (\sim K_c^4) \) as the applied load (and crack size) increases. This phenomenon is demonstrated though Vickers microindentation on Si and alloy H at various loads (Fig. 4.10). At a low indentation load 100 g \( (\sim 1N) \), indications of mild lateral fracture (i.e. microfracture) are found in both silicon (Fig. 4.10a), as interference fringes, and alloy H (Fig.
4.10b). Thus, under very small loads (i.e. small crack sizes), toughening mechanisms are not activated in the composite and the material toughness response is akin to that of a single phase material. This agrees with the observation that both silicon and the composites displayed similar wear rates under the 1 N load (Fig. 4.7). At a higher load of 300 g (~ 3 N), a very distinct difference is seen in the fracture behavior displayed by silicon (Fig. 4.10c) and alloy H (Fig. 4.10d). Here, the cracks are long enough to interact with multiple disilicide reinforcements in the composite, resulting in a rising apparent toughness. That is, crack deflection and bridging mechanisms present in the composite lead to the prevention of lateral crack propagation to the surface of the material – such mechanisms are absent in the silicon microstructure.

Figure 4.10: Effects of microstructural toughening on the formation of lateral cracks due to asperity sliding contact is modeled by Vickers indentation at various loads. At a low load of $W = 1\, \text{N}$, the extent of lateral fracture is not large enough to activate toughening mechanisms such as crack bridging – thus causing (a) unalloyed Si and Si-(Cr,V)Si$_2$ composites such as (b) alloy H to display the same wear behavior. At a higher load of $W = 3\, \text{N}$, lateral fracture is large enough to activate toughening mechanisms in the Si-(Cr,V)Si$_2$ composites, resulting in much more extensive material removal in (c) Si than compared to composites such as (d) alloy H. This helps to explain the large difference in wear rates measured for the materials at high loads (Fig. 4.7)
The effect of a rising R-curve behavior on the apparent threshold for lateral fracture can be illustrated analytically by defining an R-curve relation for the composites [i.e., $K_c = K_c(a)$] and implicitly solving Eq. 4.5b at various loads. An arctan function proposed by Evans [170] may be used to define the R-curve as follows:

$$K_R = K_0 + \frac{2}{\pi} (K_{\text{max}} - K_0) \tan^{-1} \left[ \frac{a}{\lambda} \right]$$  \hspace{1cm} (4.7)

where $K_0$ is the initial (single phase) toughness, $K_{\text{max}}$ is the maximum toughness, and $\lambda$ is the microstructural characteristic spacing. For the composites, these terms will be defined as $K_0 = 1.00 \text{ MPa} \cdot \text{m}^{1/2}$ (fracture toughness of silicon), $K_{\text{max}} = 2.45 \text{ MPa} \cdot \text{m}^{1/2}$ (mid-range long-crack toughness value for the composites reported in Table 3.4), and $\lambda = 5 \mu\text{m}$. The material-independent constant, $\alpha_1$, in Eq. 4.5b is taken as $2 \cdot 10^{-2}$ based on calibration with the lateral crack sizes observed for Si during Vickers indentation (Fig. 4.10a,c). Introducing $K_R$ (Eq. 4.7) into Eq. 4.5b for $K_c$ and implicitly solving for $a$ at various loads gives relations listed in Table 4.5. The $K_R$ curve as a function of $a^L$ is plotted in Fig. 4.11.

<table>
<thead>
<tr>
<th>Load</th>
<th>$a^L$ (μm)</th>
<th>$K_R$ (MPa·m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.18</td>
<td>1.52</td>
</tr>
<tr>
<td>2</td>
<td>5.85</td>
<td>1.80</td>
</tr>
<tr>
<td>3</td>
<td>8.41</td>
<td>1.95</td>
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<tr>
<td>4</td>
<td>10.94</td>
<td>2.05</td>
</tr>
<tr>
<td>5</td>
<td>13.46</td>
<td>2.12</td>
</tr>
<tr>
<td>6</td>
<td>15.97</td>
<td>2.17</td>
</tr>
<tr>
<td>7</td>
<td>18.48</td>
<td>2.21</td>
</tr>
<tr>
<td>8</td>
<td>20.98</td>
<td>2.23</td>
</tr>
<tr>
<td>9</td>
<td>23.49</td>
<td>2.26</td>
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<tr>
<td>10</td>
<td>25.99</td>
<td>2.27</td>
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<tr>
<td>11</td>
<td>28.50</td>
<td>2.29</td>
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<tr>
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<td>31.00</td>
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<tr>
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<td>36.01</td>
<td>2.32</td>
</tr>
<tr>
<td>15</td>
<td>38.52</td>
<td>2.33</td>
</tr>
</tbody>
</table>
Figure 4.11: Calculated R-curve for Si-(Cr,V)Si₂ alloys as a function of the limiting lateral crack size as implicitly solved through Eq. 4.5b. An arctan R-curve relation [170] was used for this derivation, with the listed parameters being estimated values based on experimental observations.

From the determination of the R-curve above, the critical load to initiate fully developed lateral cracks can be determined as a function of applied load through the threshold equation (Eq. 4.6) by using the relations given in Table 4.5 and the hardness values listed in Table 4.4 (Fig. 4.12). For unalloyed Si, which has a single-value toughness ($K_c = 1.0 \text{ MPa}\cdot\text{m}^{1/2}$), the threshold load is constant ($W_c = 0.23 \text{ N}$) and the applied load quickly exceeds the critical load to initiate lateral fracture in this material. For the Si-(Cr,V)Si₂ alloy, however, the applied load does not surpass the critical load until $W = 5 \text{ N}$ (marked as $W^*$ in Fig. 4.12). These calculations agree well with the experimental finding that Si and the Si-(Cr,V)Si₂ alloys show a substantial increase in wear rate at $W > 1 \text{ N}$ and $W > 4 \text{ N}$, respectively (Fig. 4.7). It is important to note that at the onset of lateral fracture ($W = 5 \text{ N}$), the calculated toughness is shown to be $2.12 \text{ MPa}\cdot\text{m}^{1/2}$ (Table 4.5), which is about 87% of the defined maximum toughness of $2.45 \text{ MPa}\cdot\text{m}^{1/2}$. Thus, in general, the peak fracture toughness of the composites is unlikely to be realized during the wear experiments due to the more slowly rising upper region of the R-curve. This means that the short-crack toughness is the more pertinent property in terms of governing the wear resistance.
For the Si-(Cr,V)Si₂ alloys, the critical load increases with applied load due to their increasing toughness with lateral crack size (see Fig. 4.11). This is in contrast to Si for which the critical load is a constant due to its flat R-curve behavior. As a result, the threshold for lateral fracture (W*), where W > Wᵣ, is much higher for the Si-(Cr,V)Si₂ composites than for Si.

Finally, having determined the critical loads, the actual lateral crack sizes (a) can be calculated based on Eq. 4.5a. From these calculations, the wear rates are determined from the relations [153]:

$$V = \alpha_3 \cdot 2ha$$

$$h = \left( \frac{W}{H} \right)^{1/2} \left( \frac{E}{H} \right)^{2/5}$$

where V is the normalized wear rate, h is the lateral crack depth, and a is the lateral crack length (same as Eq. 4.5a). This derivation is the same as that shown in Eq. 4.4 except that now a is a function of load (Eq. 4.5a) instead of using Eq. 4.5b which assumes W>>Wᵣ such that a ≈ aᴸ.
The material independent constant was determined to be $\alpha_3 = 5 \cdot 10^{-4}$ by fitting the calculated wear rates for unalloyed Si to the experimental values. In Fig. 4.13, the calculated wear rates (solid lines) as a function of load are plotted along with the experimental measurements from Fig. 4.7 with the data for alloy H taken for the Si-(Cr,V)Si$_2$ alloys. Good correlation between the experimental ($V_{\text{exp}}$) and calculated ($V_{\text{calc}}$) wear rates is observed for both Si and the Si-(Cr,V)Si$_2$ alloys (note that for the alloys $V_{\text{calc}} = 0$ for $W < 5$ N because $W < W_c$ as shown in Fig. 4.12). This demonstrates the ability of the lateral fracture model to accurately characterize the wear rates of the Si-(Cr,V)Si$_2$ alloys through the incorporation of a crack-size dependent functionality (i.e. R-curve) in the fracture toughness of these materials.

![Figure 4.13:](image)

**Figure 4.13:** Calculated and experimental wear rates for Si and Si-(Cr,V)Si$_2$ alloys. By incorporating an R-curve relation for the fracture toughness of the Si-(Cr,V)Si$_2$ alloys, the lateral fracture model is able to account for the microstructural toughening effects on fracture-induced wear and accurately predict the wear behavior of both flat and rising R-curve materials.
4.4.3 Testing for grain size effects on wear in silicon

In the above analysis of fracture-dominated wear, it was assumed that the microstructural scale of each of the materials analyzed was on the order of the length of lateral fracture so that the macroscopic fracture toughness of the materials was realized during the experiments. In other words, the lateral cracks were assumed to interact with microstructural features such as grain boundaries, second phase particles, etc. that may have provided resistance to lateral crack propagation. Given the extremely large grain size (order $10^2 \sim 10^3 \mu m$) of the MG silicon tested in the present study (Fig. 4.2a), it was important to test a more fine-grained silicon sample to confirm the microstructural independence of the wear behavior of this material. To do this, a fine-grained (grain size, $d_g \approx 1 - 10 \mu m$) polycrystalline sample (Fig. 4.11) was tested under the same experimental conditions at a 3N load. The resulting wear rates for the large-grained silicon and fine-grained silicon were found to be $5.20 \times 10^{-4} \pm 2.86 \times 10^{-5}$ mm$^3$/m and $5.28 \times 10^{-4} \pm 3.30 \times 10^{-5}$ mm$^3$/m, respectively. Since these values are equal to within uncertainty, it is concluded that the microstructural scale of silicon does not affect the wear response of this material. This is in agreement with previous studies of silicon that show the fracture toughness of polycrystalline silicon is independent of grain size (Table 1.2).

Figure 4.14: Microstructure of a fine-grained polycrystalline Si specimen ($d_g \approx 1 - 10 \mu m$) for which wear testing was performed at 3 N using the same experimental procedure as described in Section 4.2.2. The wear rate measured for this specimen was the same as the coarse-grained Si specimen (Fig. 4.2a) tested at the same load – indicating the microstructural independence of the wear response of unalloyed Si. The absence of a grain-size effect on the wear behavior of silicon agrees with previous studies which show that the fracture toughness of Si is independent of its microstructure. (Silicon etched with 200 mL distilled H$_2$O and 100 g NaOH)
4.5 Concluding Remarks

Tribological studies of the wear response of in-situ toughened Si-(Cr,V)Si$_2$ alloys during dry sliding show that the microstructural features that enhanced the long-crack toughness of these composites (Chapter 3) also improve their wear resistance when material removal is dominated by large-scale fracture events (i.e. severe wear). Specifically, crack bridging mechanisms are activated in the composites during abrasive wear which inhibit lateral cracks from propagating and forming wear debris during the sliding action of second- or third-body asperities across the specimen surface. In fact, the wear rate constant of the Si-(Cr,V)Si$_2$ alloys ($\approx 10^{-14}$ m$^2$/N) were found to be about an order of magnitude lower than that of unalloyed Si ($\approx 10^{-13}$ m$^2$/N) within the severe wear regime – putting the wear properties of these materials into the same range as those typically displayed by technical engineering ceramics.

Good linear fits to the wear data based on the lateral fracture model (for data taken above the critical loads needed to induce lateral fracture) indicate that the lateral fracture mechanism is the dominant mode of wear for the given testing conditions (Fig. 4.8). Despite the good fit of the wear data to the lateral fracture model, the lines of best fit for the Si-(Cr,V)Si$_2$ alloys did not extrapolate back to the origin (i.e. to $V = 0$ mm$^3$/m at $W = 0$ N) as they did for unalloyed Si. Such a discrepancy, which has been noted in other studies [157, 158], exposes the necessity to take into account the effects of microstructural toughening on the wear resistance of materials displaying rising R-curve behaviors. For the Si-(Cr,V)Si$_2$ alloys, events such as crack bridging lead to an increasing toughness with crack size. Since the crack size increases with increasing load, the apparent toughness of the alloys simultaneously increases with load, thereby requiring additional loading to initiate fully developed lateral cracks. The ability of the Si-(Cr,V)Si$_2$ alloys to display a rising R-curve behavior during wear is related to the fine microstructural scaling of these materials compared to the lateral crack size [i.e. lateral cracks ($\sim 10^0 - 10^1$ μm) are on the order of or larger than the eutectic disilicide spacing ($\sim 10^0$ μm)]. In many ceramics, where much larger crack extensions are necessary to experience a rising R-curve (e.g. a heterogeneous coarse-grained ceramic), the wear behavior will still be determined by its initial, or single crystal, toughness value ($K_0$). The ability of Si-(Cr,V)Si$_2$ microstructures to positively contribute to both the short- and long-crack response of these alloys provides an advantage over other in-situ
ceramics where microstructural toughening is achieved at the expense of degrading the wear properties of the material [159-162].
Conclusions

Up until now, silicon has been essentially disregarded as a bulk structural material due to its inherently brittle nature and apparent inability to be toughened through most typical microstructural engineering techniques. In this thesis, a new class of castable Si-rich alloys was developed which takes advantage of the desirable properties of silicon (i.e. low density, high hardness, high compressive strength, and low cost) while improving upon its fracture toughness via the in-situ formation of a composite-like microstructure during alloy solidification. Specifically, this thesis focused on the development of in-situ toughened silicon-disilicide composites in which a microstructure composed of a silicon matrix and reinforcing disilicide phase is formed though the eutectic reaction between silicon and additional alloying metal(s) (particularly transition metal(s)). The remainder of this section summarizes the significant conclusions drawn from this thesis work.

In Chapter 1, the material selection process for the development of in-situ toughened Si-rich alloys was reviewed. The foundation for the material selection was based on well established composite design theories used in the development of brittle-brittle ceramic composites. The general goal of these design techniques is to promote various toughening mechanisms in the composite by introduction of specific microstructural features or phases. For silicon-disilicide composites, alloy design was based on crack deflection and crack-bridging mechanisms, the latter of which contributes to the overall composite toughness as described by Eq. 1.8, which is reproduced below:

\[
K_{ec}^c = \left[ E^c J^m + V^el \left( \sigma_f^l \right)^2 \frac{E^c r^l}{12 E^l} \frac{\gamma^l}{\gamma^l} \right]^{1/2}
\]

Here, the second term within the brackets is associated with the increase in fracture toughness due to the elastic bridging process. Taking into account all of the parameters in the elastic bridging term, the Si-TaSi2, Si-CrSi2, Si-TiSi2, and Si-CoSi2 eutectic systems were chosen as the most viable candidates from which to develop in-situ toughened silicon-rich alloys due to the
large volume fractions ($V_{\text{eff}}$) of disilicide phase formed during the respective eutectic reactions (Table 1.5), the relatively high composite to reinforcement modulus ratio ($E'/E_i$) calculated based on a rule of mixtures (Table 1.6), and the expected weak interfaces (high $\gamma_f'/\gamma_i'$ ratio) due to large residual tensile stresses between the silicon and disilicide phases (Table 1.7). Of the four primary candidate systems, the Si-CrSi$_2$ eutectic alloy had the additional advantages of having a low density, low material costs, and the most alloying potential with other silicon-disilicide eutectic systems – particularly those forming disilicides with the same C40 crystal structure as CrSi$_2$. With respect to this last point, the Si-VSi$_2$ system was chosen as a potential candidate in addition to the Si-CrSi$_2$ system since VSi$_2$ has an even lower density than CrSi$_2$ and, having the same C40 crystal structure, is completely soluble with CrSi$_2$ throughout the entire composition range. Working within the Si-CrSi$_2$-VSi$_2$ ternary system enabled more control over the final microstructure and morphology of the Si-(Cr,V)Si$_2$ alloys by being able to tailor the volume fraction of the (Cr,V)Si$_2$ disilicide phase (by changing the Cr:V ratio) formed during eutectic solidification. In order to accurately predict how the alloy composition affects the alloy solidification paths, and thus their resulting phase constitution, a phase diagram for the Si-CrSi$_2$-VSi$_2$ system was determined in Chapter 2. In Chapters 3 and 4, microstructural analysis of the alloys was performed and compared to that predicted from the equilibrium phase diagram. Additionally, the effects of the alloy microstructure and eutectic morphology on the fracture (Chapter 3) and wear properties (Chapter 4) of the in-situ toughened Si-(Cr,V)Si$_2$ alloys was investigated, as described below.

In Chapter 2, a combined experimental-computational approach was taken to determine and verify the Si-rich corner of the Si-Cr-V phase diagram (i.e. the Si-CrSi$_2$-VSi$_2$ system). Differential scanning calorimetry and complimentary microstructural analysis was used to experimentally determine various compositions along the univariant eutectic curve connecting the Si-CrSi$_2$ and Si-VSi$_2$ binary invariant eutectic points. Enthalpies of melting and liquidus temperatures were also determined from the endothermic peak signals given off during DSC testing of the alloys. Using the CALPHAD approach, the Si-CrSi$_2$-VSi$_2$ phase diagram was also calculated using slightly modified thermodynamic descriptions [136, 141, 142] of the various binary systems (i.e. Si-Cr, Si-V, and Cr-V). Very good agreement was found between the experimental and calculated eutectic boundary curves, with the largest deviation being 2.5 at. %
Si for the binary Si-CrSi$_2$ eutectic point. The measured melting temperatures and computed liquidus curves were also consistent with one another. Having verified the thermodynamic descriptions of the Si-CrSi$_2$-VSi$_2$ system with the experimental data, equilibrium solidification paths were simulated for the alloy compositions studied in Chapters 3 and 4. For all of the alloys, the measured fraction of disilicide phase was a bit lower (~1 – 7 %) than expected from the equilibrium calculations (Tables 3.3 and 4.3). This difference is partially associated with microstructural variation within the samples caused by solute segregation during non-equilibrium solidification. Differences may also be due to tramp elements (ex. Ca, Fe, Al) in the 99.98 % Si used to make the castings which were not present in the 99.999 % Si used in the DSC experiments.

Long-crack fracture properties of near-eutectic Si-(Cr,V)Si$_2$ alloys were analyzed in Chapter 3 using chevron-notched beam (CNB) experiments. On average, the fracture toughness increased with increasing volume fractions of the disilicide phase, ranging from 2.06 ± 0.36 MPa·m$^{1/2}$ for binary Si-VSi$_2$ alloy A ($V_f^{\text{MSi}_2} = 6.7 \%$) to 2.61 ± 0.15 MPa·m$^{1/2}$ for binary Si-CrSi$_2$ alloy D ($V_f^{\text{MSi}_2} = 31.3 \%$). This correlation, which is expected from Eq. 1.8, was due to the increasing degree of crack-microstructure interactions with higher volume fractions of the reinforcing phase. These interactions were directly observed during in-situ CNB testing of the alloys, where crack deflection and subsequent bridging were found to lead to stable crack extension (beyond that expected simply from the chevron geometry) and visible crack opening displacement. Such behavior is indicative of a rising R-curve where the fracture toughness increases with advancing crack growth. Despite not having the highest volume fraction of the disilicide phase, the maximum fracture toughness was actually found to be displayed by ternary alloy B ($V_f^{\text{MSi}_2} = 19.9 \%$) for which $K_{\text{IVb}} = 3.05$ MPa·m$^{1/2}$. The ability of this alloy to display a higher fracture toughness than other alloys with larger fractions of the reinforcing disilicide phase is related to the enhanced isotropy in its toughness from having a more irregular eutectic morphology. Increasing volume fractions of the disilicide phase were observed to promote more aligned anomalous eutectic microstructures (Figs. 3.5-3.9), with alloy D displaying the most aligned, colony type microstructure. Alignment of the reinforcing phase induces highly anisotropic fracture properties in the composite, and can lead to poor fracture resistance if the eutectic
structure is aligned in a direction parallel or near-parallel to the crack propagation direction (Fig. 3.17). The irregular nature of anomalous eutectic structures for alloys with lower minor phase volume fractions (such as alloy B) leads to a wider distribution of reinforcement orientations, and thus prevents potential low-energy fracture paths from existing (assuming primary or overgrowth of the Si phase is avoided).

Taking the measured fracture toughness values (Table 3.4) and densities of the alloys using a rule of mixtures (with the phase volume fractions from Table 3.3 and densities from Table 1.3), the properties of the in-situ toughened Si-(Cr,V)Si$_2$ composites can be plotted over the Ashby chart shown in the beginning of the thesis (as motivation for this work) which compares the specific compressive strength and fracture toughness of silicon and commonly used technical ceramics (Fig. 5.1). By more than doubling or tripling the fracture toughness of silicon (K$_{IC} = 0.8 – 1.0$ MPa·m$^{1/2}$) without increasing its density ($\rho = 2.33$ g/cm$^3$) by nearly the same amount (maximum $\rho = 3.40$ g/cm$^3$ for alloy D specimens with $V_f^{Si} = 39.6 \%$), the specific fracture toughness of the alloys fall well within the range of values displayed by many powder-processed engineering ceramics. Here, it is assumed that the compressive strengths of the composites are of a similar magnitude to that displayed by silicon; in reality, they are expected to be even larger due to enhanced flaw tolerance of the composites.
Figure 5.1: Ashby plot of specific fracture toughness \( (K_{IC}/\rho) \) versus specific strength \( (\sigma_f/\rho) \). By more than doubling or tripling silicon’s fracture toughness without greatly increasing its density, in-situ toughened Si-(Cr,V)Si\(_2\) composites can achieve specific strength and toughness values within the same range as those displayed by most engineering ceramics.

In Chapter 4, the tribology of unalloyed Si and Si-(Cr,V)Si\(_2\) alloys during sliding wear was studied using a ball-on-disk method (WC counterbody) to assess whether the microstructural toughening observed to enhance the long-crack fracture toughness of these materials (Chapter 3) also improved their wear resistance. For testing conditions under which wear was dominated by lateral fracture, it was found that the wear rate constant of the Si-(Cr,V)Si\(_2\) alloys \( (\approx 10^{-14} \text{ m}^2/\text{N}) \) were about an order of magnitude lower than that of unalloyed Si \( (\approx 10^{-13} \text{ m}^2/\text{N}) \). This magnitude of the wear rate constants found for the composites are typical of those displayed by engineering ceramics, cermets, and nitrided steels (Fig. 5.2). The improvement in the short-crack wear behavior of the alloys was linked to the crack deflection and bridging mechanisms observed during the long-crack response in the CNB tests. Due to the enhanced short-crack fracture toughness of the alloys, the critical load necessary to induce severe wear \( (W_c = 4 \text{ N}) \) was found to be four times greater than that measured for unalloyed silicon \( (W_c = 1 \text{ N}) \). Evidence of a rising R-curve behavior for the alloys was noted by the fact that the wear rate \( (V) \) data fitted to the lateral fracture model (for \( W > W_c \)) did not pass through the origin, despite following the
linear relationship predicted by the model \( V \propto \frac{1}{K_c^{1/2}} \) (Fig. 4.8). The discrepancy found between the lateral fracture model and the experimental wear data was explained by the necessity to take into account the crack-size dependence of the alloy fracture toughness as defined by a rising R-curve behavior. The ability of the microstructure of in-situ toughened Si-(Cr,V)Si\(_2\) alloys to simultaneously enhance the wear and fracture toughness of these materials compared to the unalloyed Si matrix, indicates that these composites have the potential to be used as reliable structural components for applications where both the short-crack and long-crack response of the material govern the operating lifetime of the component.

**Figure 5.2:** Ashby plot of the dry wear rate constant (i.e. wear rate) versus hardness. An order of magnitude improvement in the wear rate constant of the Si-(Cr,V)Si\(_2\) alloys (~ \(10^{-14}\) m\(^2\)/N) over the unalloyed Si matrix (~ \(10^{-13}\) m\(^2\)/N) puts the wear properties of this new class of alloys in the same regime as those displayed by some engineering ceramics, cermet, and nitried steels – all of which are used as tribological components in applications where abrasive wear is a concern. It should be noted that the wear rate constants shown in the plot are given for operating pressures that are a fraction of the maximum bearing pressure \( (P/P_{max}) \) for a given material such that \( k_a \) is a true constant (i.e. does not increase with increasing load). The maximum bearing pressure is proportional to the hardness of the material. (Image adapted from [171])
Directions for future work

The present work represents the foundation and initial progress that has been made in the development of a new class of castable, in-situ toughened Si-rich alloys. As with the emergence of any new field of research, there are still many scientific and technological aspects that need to be considered before for such a technology can fully mature. Therefore, the author suggests some of the following topics as directions for which to direct future research efforts:

- In Chapter 1, the foundation for the material selection process was based on the formation of brittle-brittle type composites composed of a silicon matrix and a reinforcing disilicide phase. Although the Si-CrSi$_2$-VSi$_2$ system was chosen as the basis from which to develop and characterize the presently studied in-situ toughened Si-(Cr,V)Si$_2$ composites, there is reason to believe that other silicon-disilicide systems (particularly those described in Chapter 1) can achieve similar mechanical properties. Thus, simple extensions of the experimental platform described in this thesis to incorporate other binary and higher order silicon-disilicide systems is recommended to broaden the scope of knowledge on the microstructural and mechanical properties of this new class of materials.

- Toughening in Si-(Cr,V)Si$_2$ composites has been shown to occur by crack deflection and bridging mechanisms. However, even with these types of toughening mechanisms, the maximum toughness attainable in these materials is limited by lack of ductility displayed by both the silicon and disilicide phases. To further increase the toughness of such brittle-brittle composites, it is recommended that additional types of toughening be sought in the composites through further modification of the alloy microstructure. For instance, a ductile phase may be introduced into the alloy microstructure through use of material system in which additional alloying elements to the silicon-disilicide system do not form intermediate compounds with either silicon or the transition metals. Two examples are shown in Fig. 6.1 for a Si-CrSi$_2$ binary alloy with small additions of Ag (Fig. 6.1a) and Sn (Fig. 6.1b). For the first case, it is known that Ag forms a single eutectic with Si at around 2.5 wt. % Si and forms a miscibility gap with Cr over the entire composition range. During solidification of a Si-rich alloy within the Si-Cr-Ag system, Ag forms a low melting eutectic with Si that is
located either within the Si-CrSi$_2$ eutectic structure or at the eutectic boundaries (Fig. 6.1a).

In this alloy, the Si-Ag eutectic structure would provide the ductile phase toughening. For the second case, Sn forms a miscibility gap with Si over the entire composition range (i.e. the eutectic composition is of negligible Si content) and is soluble in chromium up to a concentration of about 4.5 wt. % Sn; above this, it is immiscible with Cr. During solidification of a Si-rich alloy within the Si-Cr-Sn system, Sn is rejected from the eutectic Si and CrSi$_2$ crystals and segregates to the boundaries of the Si-CrSi$_2$ eutectic colonies (Fig. 6.1b). In this alloy, Sn provides ductile phase toughening through mechanisms such as crack arrest (Fig. 6.1c).

![Figure 6.1](image_url)

**Figure 6.1:** (a) During solidification of a Si-CrSi$_2$ alloy with Ag additions [Si-17.7Cr-6.7Ag (wt.%)], Ag forms a low melting eutectic with Si that solidifies within the Si-CrSi$_2$ eutectic structure or at the eutectic boundaries. (b) During solidification of a Si-CrSi$_2$ alloy with Sn additions [Si-17.6Cr-7.3Sn (wt.%)], Sn is rejected from Si and CrSi$_2$ crystals that grow during Si-CrSi$_2$ eutectic growth and solidifies at the boundaries of the Si-CrSi$_2$ eutectic colonies. At the eutectic boundaries, the Sn phase will provide ductile phase toughening mechanisms such as crack arrest as shown in (c) during Vickers indentation (100 g) performed on the alloy.
In Chapter 2, the thermodynamic description of the Si-CrSi$_2$-VSi$_2$ ternary phase diagram (Table B.1 of the appendix), was used to predict the equilibrium solidification paths of several Si-(Cr,V)Si$_2$ alloys studied in this work. It was found that the phase volume fractions expected from these simulations differed from the measured values due to microstructural variation in the cast alloys caused by non-equilibrium solidification conditions. To more closely predict the solidification sequence of these alloys, one may try to take segregation effects into account by implementing Scheil simulations which assume negligible diffusion is the solid phase and perfect mixing in the liquid during solidification. However, even more precise solidification simulations can be made using the DICTRA® (Diffusion Controlled TRAnsformations) software coupled with the Thermo-Calc ® program used in the current work. The DICTRA® software takes kinetic properties (i.e. diffusion coefficients, atomic mobilities, etc.) of the relevant species into account in order to simulate complex diffusion processes such as microsegregation. Additionally, phenomena such as alloy homogenization and microstructural coarsening can be modeled – both of which may be of significant importance during production and application of Si-(Cr,V)Si$_2$ and related in-situ toughened Si-rich alloys.

In Chapter 3, it was found that the improved fracture toughness of Si-(Cr,V)Si$_2$ alloys over unalloyed Si was due to microstructural toughening in the composites materials, including crack deflection and bridging mechanisms. These mechanisms lead to a rising R-curve behavior where the fracture toughness of the composite actually increases with increasing crack size. In engineering ceramics, it has been found that a rising R-curve behavior also tends to lead to an increase in strength [102, 172] and a decrease in the scatter of the strength [102, 172]. The improvement in strength variability for materials displaying a rising R-curve behavior is related to the fact that the fracture strength of these materials are insensitive to flaw size in the stable-crack regime (i.e. $\partial K / \partial a < dK_R / da$, where $K$ is the stress intensity and $K_R$ is the fracture toughness of the material defined by the R-curve). On the other hand, the fracture strengths of materials with flat R-curves continuously decrease with crack size. Thus, it is of interest to measure the compressive strengths of the Si-(Cr,V)Si$_2$ alloys to see whether or not the observed toughening in these materials leads to higher fracture strengths and decreased strength variability; the latter of which can be measured using a Weibull
analysis. Also, as discussed in Chapter 3, the eutectic morphology of the Si-(Cr,V)Si₂ alloys strongly affects the isotropy in the fracture toughness of these materials – the more aligned structures displaying more anisotropic fracture properties. Thus, a related study should also be done on the effects of eutectic morphology on the variability of the fracture strength of these alloys.

- Study of the temperature dependence of the mechanical properties, including fracture toughness, of Si-(Cr,V)Si₂ alloys is important for these materials to be reliably used at elevated temperatures. Properties such as the brittle-to-ductile transition temperature (BDTT) should be measured to understand the temperature dependence of the composite fracture strength and how that dependence differs from the sharp brittle-to-ductile transitions displayed by the individual constituent phases. In terms of wear applications, severe temperature effects can be induced by the actual operating environment, very rapid sliding speeds, large loads, or even by a change in the tribosystem (specifically changes in the mechanical and thermal properties of the counterbody). Examples of some temperature effects which can lead to accelerated wear rates are increased friction, chemical reactions (with environment or counterbody), thermal shock, and decreased material hardness. Thus, wear testing of the Si-(Cr,V)Si₂ alloys should be performed under similar operating conditions as their intended application, as to ensure that such temperature effects will not affect the enhanced wear resistance of the composites that were measured under the testing conditions described in this work. Finally, the oxidation resistance of Si-(Cr,V)Si₂ and related alloys should be measured if these materials are to be used at elevated temperatures under reactive (non-inert) environments.

- One of the key advantages of having castable (versus powder processed) in-situ toughened composites is that such alloys are amenable to many different high-volume processing routes such as die casting, sand casting, investment casting, etc. Each of the routes should be studied as a means to which to feasibly produce the Si-(Cr,V)Si₂ alloys with desired microstructural and mechanical properties. As a proof of concept for the Si-rich alloys to be processed by investment casting, medallions containing the MIT university logo were processed using this method with alloys composed of Si-20.29Cr (wt.%) (Fig. 6.2).
intricate details of the logo that are captured in these medallions would be very difficult to achieve via powder processing routes which would require complicated molds and pressing fixtures. A feasibility study of the various processing methods should also include a cost-benefit analysis to compare the material, processing, and associated labor costs of the castable Si-rich alloys with typical powder processed engineering ceramics.

Figure 6.2: Photograph of an MIT medallion that was produced through an investment casting process with a Si-20.29Cr (wt.%) alloys. The intricate details captured in the medallion demonstrates the advantage of the castable Si-rich alloys over powder-processed ceramics of being able to be easily processed into complicated geometries. The dimensions of the medallions were diameter = 6 cm and thickness = 0.6 cm.
Appendix A: Design of DSC experiments

In designing the differential scanning calorimetry experiments (Chapter 2), it was important to ensure complete homogenization of the alloy, while at the same time, minimize the extent of chemical reaction between the alloy and Al₂O₃ sample pan at the elevated processing temperatures. To reduce the time the molten alloy was in contact with the pan, the minimum amount of time required to isothermally hold the alloy above its melting temperature and achieve complete mixing was determined. Figure A.1 shows the thermal signal of the raw materials (41.2 mg) for an alloy [Si-13.00Cr (at. %)] melted at 1600 °C for 60 min under a flowing argon atmosphere. At the start of melting, a large drop in heat flow is observed which corresponds to the endothermic melting reactions of the raw materials. Some exothermic peaks are also present which may be due to reactions between the alloy constituents or with the sample pan. After about 30 min, the heat flow curve seems to plateau, indicating that the melting process has been completed. Therefore, an isothermal holding time of 30 min at 1600 °C was used for the melting stage of the thermal cycles used in the DSC experiments of this work.

![Figure A.1: DSC thermal signal measured during the isothermal melting stage (T = 1600 °C) for a Si-13Cr (at. %) alloy. The curve levels off after about 30 min indicating that melting of the raw materials is completed.](image-url)
To verify that the 30 min melt time was short enough to prevent any significant reactions between the specimen and Al$_2$O$_3$ sample pan from occurring, a pure silicon specimen (99.999 % granular Si) was tested using the same thermal cycle as for the Si-(Cr,V)Si$_2$ alloys. After the melting and subsequent quenching stages, the specimen was reheated at 5 °C/min during which time the melting temperature and enthalpy of melting were measured (Fig. A.2). The measured melting temperature ($T_m = 1414$ °C) and enthalpy of melting ($\Delta H_m = 48.7$ kJ/mol) for silicon agreed extremely well with values reported in literature ($T_m = 1414$ °C, $\Delta H_m = 50.2$ kJ/mol [173]). Thus, the extent of reaction (if any) with the Al$_2$O$_3$ pan during melting was not significant enough to contaminate the silicon specimen as to alter its thermal properties during melting. Therefore, the methodology used for the DSC experiments in this work was deemed acceptable.

![DSC curve for a pure silicon specimen](image)

**Figure A.2:** DSC curve for a pure silicon specimen that was processed and analyzed using the same experimental procedure as for the Si-(Cr,V)Si$_2$ alloys (see Section 2.2.1). The melting temperature ($T_m$) and enthalpy of melting ($\Delta H_m$) measured for silicon (shown on graph) agreed extremely well with those reported in literature, thereby demonstrating the minimal extent to which the silicon was contaminated by reaction with the Al$_2$O$_3$ sample pan during melting.
Appendix B: Thermodynamic parameters of the Si-Cr-V system and experimental thermodynamic data for selected alloys

Table B.1: Summary of thermodynamic parameters in the Si-Cr-V system

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>REF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid: (Cr, Si, V)</td>
<td></td>
</tr>
<tr>
<td>$0 L_{\text{Liquid}}^{\text{Cr,Si}}$</td>
<td>$-126,112.28 + 19.92557 \cdot T$ [142]</td>
</tr>
<tr>
<td>$1 L_{\text{Liquid}}^{\text{Cr,Si}}$</td>
<td>$-48,048.45 + 11.38497 \cdot T$ [142]</td>
</tr>
<tr>
<td>$0 L_{\text{Liquid}}^{\text{Cr,V}}$</td>
<td>$-9,874 - 2.6964 \cdot T$ [136]</td>
</tr>
<tr>
<td>$1 L_{\text{Liquid}}^{\text{Cr,V}}$</td>
<td>$-1,720 - 2.5237 \cdot T$ [136]</td>
</tr>
<tr>
<td>$0 L_{\text{Liquid}}^{\text{Si,V}}$</td>
<td>$-190,326.8 + 44.06262 \cdot T$ [141]</td>
</tr>
<tr>
<td>$1 L_{\text{Liquid}}^{\text{Si,V}}$</td>
<td>$6,265.4$ [141]</td>
</tr>
<tr>
<td>$2 L_{\text{Liquid}}^{\text{Si,V}}$</td>
<td>$39,546.5$ [141]</td>
</tr>
<tr>
<td>BCC-A2: (Cr, Si, V)$_1$(Va)$_1$</td>
<td></td>
</tr>
<tr>
<td>$0 L_{\text{bcc-A2}}^{\text{Cr,Si/Va}}$</td>
<td>$-104,537.94 + 10.69527 \cdot T$ [136]</td>
</tr>
<tr>
<td>$1 L_{\text{bcc-A2}}^{\text{Cr,Si/Va}}$</td>
<td>$-47,614.7 + 12.17363 \cdot T$ [136]</td>
</tr>
<tr>
<td>$0 L_{\text{bcc-A2}}^{\text{Cr,V/Va}}$</td>
<td>$-9,875 - 2.6964 \cdot T$ [136]</td>
</tr>
<tr>
<td>$1 L_{\text{bcc-A2}}^{\text{Cr,V/Va}}$</td>
<td>$-1,720 - 2.5237 \cdot T$ [136]</td>
</tr>
<tr>
<td>$0 L_{\text{bcc-A2}}^{\text{Si,V/Va}}$</td>
<td>$-205,373.1 + 61.02211 \cdot T$ [141]</td>
</tr>
<tr>
<td>$1 L_{\text{bcc-A2}}^{\text{Si,V/Va}}$</td>
<td>$37,000$ [136]</td>
</tr>
<tr>
<td>$2 L_{\text{bcc-A2}}^{\text{Si,V/Va}}$</td>
<td>$20,000$ [136]</td>
</tr>
<tr>
<td>Cr$_3$Si: (Cr,$_3$Si)$_3$(Cr,Si)$_1$</td>
<td></td>
</tr>
<tr>
<td>$0 C_{\text{CrSi}}^{\text{Cr,Si}} - 4H_{\text{Cr}}^{\text{SER}}$</td>
<td>$20,000 + 10 \cdot T + 4 \cdot GHSERCR$ [142]</td>
</tr>
<tr>
<td>$0 C_{\text{CrSi}}^{\text{Cr,Si}} - H_{\text{Cr}}^{\text{SER}} - 3H_{\text{Si}}^{\text{SER}}$</td>
<td>$316,999.96 - 68.59964 \cdot T + GHSERCR + 3 \cdot GHSERSI$ [142]</td>
</tr>
<tr>
<td>$0 C_{\text{CrSi}}^{\text{Cr,Si}} - 3H_{\text{Cr}}^{\text{SER}} - H_{\text{Si}}^{\text{SER}}$</td>
<td>$-115,442.82 - 1.40036 \cdot T + 3 \cdot GHSERCR + GHSERSI$ [142]</td>
</tr>
</tbody>
</table>
\[ ^0C_{Cr\cdot Si} - 4H_{Si}^{SER} = 208,000 - 80 \cdot T + 4 \cdot GHSERSI \] [142]

\[ ^0L_{Cr\cdot Si\cdot Cr} = ^0L_{Cr\cdot Si\cdot Si} = -9,661.46 \] [142]

\[ ^0L_{Cr\cdot Si\cdot Si\cdot Cr} = ^0L_{Si\cdot Cr\cdot Si} = -16,781.4 \] [142]

\[ \alpha Cr_3Si_3: Cr_5Si_3 \]

\[ ^0G_{Cr\cdot Si} - 5H_{Cr}^{SER} - 3H_{Si}^{SER} = -316,886.2 + 1,067.79713 \cdot T - 182.578184 \cdot T \cdot LN(T) \]
\[ -0.023919688 \cdot T^2 - 2.31728 \cdot 10^{-6} \cdot T^3 \] [142]

\[ \beta Cr_3Si_3: (Cr, Si)_2(Cr, Si)_{3}(Cr)_{3} \]

\[ ^0G_{Cr\cdot Cr\cdot Si} - 8^0G_{Cr}^{SER} = 40,000 \] [142]

\[ ^0G_{Si\cdot Cr\cdot Cr} - 2^0G_{Si}^{SER} - 2^0G_{Cr}^{SER} = 276,920 + 17.7412 \cdot T \] [142]

\[ ^0G_{Cr\cdot Cr\cdot Si\cdot Cr} = ^0G_{Cr\cdot Si} = 19,359.21 - 10.78731 \cdot T \] [142]

\[ ^0G_{Si\cdot Cr\cdot Si\cdot Cr} - 5\cdot ^0G_{Si}^{SER} - 3\cdot ^0G_{Cr}^{SER} = 0 \] [142]

\[ CrSi: Cr_7Si \]

\[ ^0G_{Cr\cdot Si} - H_{Cr}^{SER} - H_{Si}^{SER} = -79,273.09 + 312.40316 \cdot T - 51.62865 \cdot T \cdot LN(T) \]
\[ -0.00447355 \cdot T^2 + 391,330 \cdot T^{-1} \] [142]

\[ CrSi_2: (Cr, Si, V)_1(Cr, Si)_2 \]

\[ ^0G_{Cr\cdot Si\cdot Si} - 3H_{Cr}^{SER} = 10,000 - T + 3 \cdot GHSERCR \] [142]

\[ ^0G_{Si\cdot Cr\cdot Si} - 2H_{Cr}^{SER} - H_{Si}^{SER} = 174,006 - 27.21105 \cdot T + 2 \cdot GHSERCR + GHSERSI \] [142]

\[ ^0G_{Cr\cdot Si\cdot Si} - H_{Cr}^{SER} - 2H_{Si}^{SER} = -100,352.65 + 336.777 \cdot T - 57.85575 \cdot T \cdot LN(T) \]
\[ -0.0132277 \cdot T^2 - 4.3203 \cdot 10^{-7} \cdot T^3 \] [142]

\[ ^0G_{Si\cdot Cr\cdot Si} - 3H_{Si}^{SER} = 82,389.75 - 24.68504 \cdot T + 3 \cdot GHSERSI \] [142]

\[ ^0G_{Cr\cdot Si\cdot Si} - 2H_{Si}^{SER} - H_{v}^{SER} = -162,308.4 + 408.29196 \cdot T - 67.8 \cdot T \cdot LN(T) \]
\[ -0.0075 \cdot T^2 + 330,000 \cdot T^{-1} \] [141]

\[ ^0G_{Cr\cdot Si\cdot Si} - 2H_{Cr}^{SER} - H_{v}^{SER} = 0.0 \]

\[ ^0L_{Cr\cdot Si\cdot Cr} = ^0L_{Cr\cdot Si\cdot Si} = 1435.7 \] [142]

\[ ^0L_{Si\cdot Cr\cdot Si} = ^0L_{Si\cdot Cr\cdot Si} = -35,879.97 + 7.17599 \cdot T \] [136]

\[ V_3Si: (Si, V)_3(Si, V)_1 \]

\[ ^0G_{Si\cdot Si\cdot Si} - 4H_{Si}^{SER} = 208,000 - 80 \cdot T + 4 \cdot GHSERSI \] [141]
\begin{align*}
0 \Delta G_{V,Si}^{V} - H_{Si}^{SER} - 3H_{V}^{SER} &= -177,099.2 + 25.88756 \cdot T + 3 \cdot GHSERV + GHSERSI \\
0 \Delta G_{Si,V}^{V} - 3H_{Si}^{SER} - H_{V}^{SER} &= 21,7099.2 - 25.88756 \cdot T + GHSERV + 3 \cdot GHSERSI \\
0 \Delta G_{V,V}^{V} - 4H_{V}^{SER} &= 20,000 + 4 \cdot GHSERV \\
0 \Delta G_{V,Si}^{V} - 0 \Delta G_{Si,V}^{V} &= -38,908.4 \\
0 \Delta G_{V,Si}^{V} - 0 \Delta G_{Si,V}^{V} &= 16,043.1 - 6.91487 \cdot T \\
\text{V}_2\text{Si}_3: \text{V}_2\text{Si}_3 & \\
0 \Delta G_{V,Si}^{V} - 3H_{Si}^{SER} - 5H_{V}^{SER} &= -443,336.8 + 53.40392 \cdot T + 5 \cdot GHSERV + 3 \cdot GHSERSI \\
\text{V}_3\text{Si}_5: \text{V}_3\text{Si}_5 & \\
0 \Delta G_{V,Si}^{V} - 5H_{Si}^{SER} - 6H_{V}^{SER} &= -580,401.8 + 65.04476 \cdot T + 6 \cdot GHSERV + 5 \cdot GHSERSI
\end{align*}

* In J/mol; temperature (T) in Kelvin. The lattice stabilities for the pure elements are taken from the SGTE compilation by Dinsdale [143] and are represented here by the symbol GHSER(i), (where i is the element Si, Cr, or V). Thus, $GHSER(i)=^0 \Delta G_{i}^{SER}(T) - H_{i}^{SER}$ (298.15 K).

**Table B.2:** Enthalpies of melting ($\Delta H_m$) and liquidus temperatures ($T_m$) for alloys in the binary Si-CrSi$_2$ system (bold composition was determined to be eutectic)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Si (at. %)</th>
<th>Cr (at. %)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g) (peak 1)</th>
<th>$\Delta H_m$ (J/g) (peak 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>96.00</td>
<td>4.00</td>
<td>1387</td>
<td>-57.33</td>
<td>-323.91</td>
</tr>
<tr>
<td>2</td>
<td>93.96</td>
<td>6.04</td>
<td>1375</td>
<td>-154.44</td>
<td>-277.77</td>
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<tr>
<td>3</td>
<td>88.80</td>
<td>11.20</td>
<td>1339</td>
<td>-661.78</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>88.20</td>
<td>11.80</td>
<td>1344</td>
<td>-694.68</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td><strong>87.91</strong></td>
<td><strong>12.09</strong></td>
<td><strong>1338</strong></td>
<td><strong>-601.61</strong></td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>87.00</td>
<td>13.00</td>
<td>1341</td>
<td>-622.00</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>86.40</td>
<td>13.60</td>
<td>1340</td>
<td>-602.62</td>
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<tr>
<td>8</td>
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<tr>
<td>9</td>
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<td>10</td>
<td>75.00</td>
<td>25.00</td>
<td>1430</td>
<td>-272.24</td>
<td>-216.84</td>
</tr>
</tbody>
</table>
Table B.3: Enthalpies of melting ($\Delta H_m$) and liquidus temperatures ($T_m$) for alloys in the binary Si-VSi$_2$ system (bold composition was determined to be eutectic)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Si (at. %)</th>
<th>V (at. %)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g) (peak 1)</th>
<th>$\Delta H_m$ (J/g) (peak 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>97.60</td>
<td>2.40</td>
<td>1395</td>
<td>-501.67</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>97.00</td>
<td>3.00</td>
<td>1394</td>
<td>-465.50</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>96.40</td>
<td>3.60</td>
<td>1385</td>
<td>-372.61</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>96.01</td>
<td>3.99</td>
<td>1386</td>
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<td>5</td>
<td>95.20</td>
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<td>-</td>
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<tr>
<td>6</td>
<td>94.00</td>
<td>6.00</td>
<td>1376</td>
<td>-554.54</td>
<td>-</td>
</tr>
</tbody>
</table>

Table B.4: Enthalpies of melting ($\Delta H_m$) and liquidus temperatures ($T_m$) for alloys in isopleth 1 (95.46 at. % Si) system (bold composition was determined to be eutectic)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr (at. %)</th>
<th>V (at. %)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g) †</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.00</td>
<td>4.54</td>
<td>1394</td>
<td>-401.32</td>
</tr>
<tr>
<td>b</td>
<td>0.23</td>
<td>4.31</td>
<td>1394</td>
<td>-507.32</td>
</tr>
<tr>
<td>c</td>
<td>0.45</td>
<td>4.09</td>
<td>1388</td>
<td>-635.88</td>
</tr>
<tr>
<td>d</td>
<td>0.91</td>
<td>3.63</td>
<td>1377</td>
<td>-616.79</td>
</tr>
<tr>
<td>e</td>
<td>1.36</td>
<td>3.18</td>
<td>1378</td>
<td>-673.90</td>
</tr>
</tbody>
</table>

Table B.5: Enthalpies of melting ($\Delta H_m$) and liquidus temperatures ($T_m$) for alloys in isopleth 2 (94.51 at. % Si) system (bold composition was determined to be eutectic)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr (at. %)</th>
<th>V (at. %)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g) †</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.55</td>
<td>4.94</td>
<td>1391</td>
<td>-490.19</td>
</tr>
<tr>
<td>b</td>
<td>1.10</td>
<td>4.39</td>
<td>1386</td>
<td>-478.01</td>
</tr>
<tr>
<td>c</td>
<td>1.65</td>
<td>3.84</td>
<td>1385</td>
<td>-457.81</td>
</tr>
<tr>
<td>d</td>
<td>2.20</td>
<td>3.29</td>
<td>1387</td>
<td>-456.09</td>
</tr>
</tbody>
</table>
Table B.6: Enthalpies of melting ($\Delta H_m$) and liquidus temperatures ($T_m$) for alloys in isopleth 3 (92.62 at. % Si) system (bold composition was determined to be eutectic)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr (at. %)</th>
<th>V (at. %)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g) †</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
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<td>4.43</td>
<td>1414</td>
<td>-594.64</td>
</tr>
<tr>
<td>b</td>
<td>3.69</td>
<td>3.69</td>
<td>1405</td>
<td>-573.07</td>
</tr>
<tr>
<td>c</td>
<td>4.43</td>
<td>2.95</td>
<td>1378</td>
<td><strong>-401.20</strong></td>
</tr>
<tr>
<td>d</td>
<td>4.80</td>
<td>2.58</td>
<td>1379</td>
<td>-453.38</td>
</tr>
<tr>
<td>e</td>
<td>5.17</td>
<td>2.21</td>
<td>1375</td>
<td>-434.44</td>
</tr>
<tr>
<td>f</td>
<td>5.54</td>
<td>1.84</td>
<td>1377</td>
<td>-458.23</td>
</tr>
<tr>
<td>g</td>
<td>5.90</td>
<td>1.48</td>
<td>1379</td>
<td>-564.05</td>
</tr>
</tbody>
</table>

Table B.7: Enthalpies of melting ($\Delta H_m$) and liquidus temperatures ($T_m$) for alloys in isopleth 4 (91.68 at. % Si) system (bold composition was determined to be eutectic)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr (at. %)</th>
<th>V (at. %)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g) †</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>2.50</td>
<td>5.82</td>
<td>1446</td>
<td>-548.63</td>
</tr>
<tr>
<td>b</td>
<td>3.33</td>
<td>4.99</td>
<td>1432</td>
<td>-501.94</td>
</tr>
<tr>
<td>c</td>
<td>4.16</td>
<td>4.16</td>
<td>1410</td>
<td>-504.41</td>
</tr>
<tr>
<td>d</td>
<td>4.99</td>
<td>3.33</td>
<td>1388</td>
<td>-545.23</td>
</tr>
<tr>
<td>e</td>
<td><strong>5.82</strong></td>
<td><strong>2.50</strong></td>
<td><strong>1372</strong></td>
<td><strong>-786.29</strong></td>
</tr>
<tr>
<td>f</td>
<td>6.66</td>
<td>1.66</td>
<td>1369</td>
<td>-629.68</td>
</tr>
</tbody>
</table>
Table B.8: Enthalpies of melting ($\Delta H_m$) and liquidus temperatures ($T_m$) for alloys in isopleth 5 (89.80 at. % Si) system (bold composition was determined to be eutectic)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr (at.%)</th>
<th>V (at.%)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)$^\dagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.02</td>
<td>9.18</td>
<td>1501</td>
<td>-431.69</td>
</tr>
<tr>
<td>b</td>
<td>2.04</td>
<td>8.16</td>
<td>1487</td>
<td>-482.78</td>
</tr>
<tr>
<td>c</td>
<td>3.06</td>
<td>7.14</td>
<td>1468</td>
<td>-474.20</td>
</tr>
<tr>
<td>d</td>
<td>4.08</td>
<td>6.12</td>
<td>1454</td>
<td>-486.21</td>
</tr>
<tr>
<td>e</td>
<td>5.10</td>
<td>5.10</td>
<td>1447</td>
<td>-356.19</td>
</tr>
<tr>
<td>f</td>
<td>6.12</td>
<td>4.08</td>
<td>1414</td>
<td>-390.49</td>
</tr>
<tr>
<td>g</td>
<td>7.14</td>
<td>3.06</td>
<td>1405</td>
<td>-408.67</td>
</tr>
<tr>
<td>h</td>
<td>8.16</td>
<td>2.04</td>
<td>1364</td>
<td>-450.28</td>
</tr>
<tr>
<td>i</td>
<td>9.18</td>
<td>1.02</td>
<td>1358</td>
<td>-402.10</td>
</tr>
<tr>
<td>j</td>
<td>10.20</td>
<td>0.00</td>
<td>1361</td>
<td>-373.77</td>
</tr>
</tbody>
</table>

Table B.9: Enthalpies of melting ($\Delta H_m$) and liquidus temperatures ($T_m$) for alloys in isopleth 6 (88.85 at. % Si) system (bold composition was determined to be eutectic)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr (at.%)</th>
<th>V (at.%)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)$^\dagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>4.46</td>
<td>6.69</td>
<td>1461</td>
<td>-493.11</td>
</tr>
<tr>
<td>b</td>
<td>5.57</td>
<td>5.57</td>
<td>1448</td>
<td>-437.81</td>
</tr>
<tr>
<td>c</td>
<td>6.69</td>
<td>4.46</td>
<td>1415</td>
<td>-499.05</td>
</tr>
<tr>
<td>d</td>
<td>7.80</td>
<td>3.35</td>
<td>1397</td>
<td>-450.28</td>
</tr>
<tr>
<td>e</td>
<td>8.92</td>
<td>2.23</td>
<td>1380</td>
<td>-410.20</td>
</tr>
<tr>
<td>f</td>
<td>10.03</td>
<td>1.12</td>
<td>1347</td>
<td>-564.69</td>
</tr>
</tbody>
</table>

$^\dagger$NOTE: $\Delta H_m$ for the ternary eutectic alloys (Tables B.4-B.9) are taken from the first melting peak which includes the melting along the eutectic boundary curve, as well as any small amounts primary melting which are not resolved from the main eutectic peak. The enthalpies for the primary phases were not calculated for these alloys because of the poorly developed peak shape which prevented accurate integration of these peaks.
References


