

# A review of directionally solidified intermetallic composites for high-temperature structural applications

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Alloys based on intermetallics have been considered for high temperature structural applications. However, many of these alloys suffer from intrinsic brittleness and low fracture toughness at ambient temperature. Therefore, ductile-phase-toughened intermetallic composites are being investigated as a means to improve the fracture toughness. A subset of this class of materials is *in-situ* composites produced by directional solidification of intermetallic eutectics. In this paper, we review recent developments related to the processing and properties of these composites. © 2004 Kluwer Academic Publishers

## 1. Introduction

With advances in high temperature technology, the need for materials with superior strength, rigidity and ductility at elevated temperatures has been growing. Nickel-based superalloys [1–6] have been among the most widely used of such materials since the second world war. However, their high temperature capability is inherently limited by the melting points of nickel (1453°C), and other lower melting constituents, such as Ni<sub>3</sub>Al [7–10], which are the principal strengthening phases in Ni-based superalloys. To meet the challenge of higher operation temperatures, alloys based on refractory intermetallics with melting points  $T_m > 1600^\circ\text{C}$  have recently been investigated, several of which have attractive properties for elevated temperature structural applications, including good oxidation resistance and creep strength [11–24]. However, many of these intermetallic compounds suffer from intrinsic brittleness and low fracture toughness at ambient temperature. Therefore, ductile-phase-toughened intermetallic composites have been investigated as a way to improve the fracture toughness. A subset of this class of materials is *in-situ* composites [19–24].

*In-situ* composites are multi-phase materials where the reinforcing phase is synthesized during composite fabrication, in contrast to *ex-situ* composites where the reinforcing phase is produced separately and then introduced into the matrix during a subsequent processing step such as infiltration or powder processing [25]. There are a number of processes for producing *in-*

*situ* composites, which can be divided broadly into two groups depending on whether the reinforcements first appear in the liquid or solid state [26]. Solid-state *in-situ* processes include internal oxidization [27], displacement reaction [28], reactive milling [29], mechanical alloying [30], and cryomilling [31]. The well known eutectoid reaction in steels can also be considered an *in-situ* solid state reaction with cementite acting as the reinforcement and ferrite as the matrix. Liquid-state processes include rapid solidification [32–36], traditional casting, and directional solidification of eutectic alloys. In this review, we restrict our discussion to just one of these processes, namely directional solidification of eutectics.

The role of eutectics in the development of ductile phase toughened intermetallic composites has been discussed by Mazdizyasni and Miracle [37]. They listed several advantages of producing *in-situ* composites by directional solidification of eutectics, specifically: directional solidification allows components to be produced from the melt in a single stage process; there is intrinsic thermodynamic stability and chemical compatibility between the matrix and reinforcements; and the microstructure can be controlled over a wide range, from well-aligned lamellae to finely dispersed particles or fibers, by adjusting the solidification conditions [21–24, 37–40]. In their work [37], several eutectic systems (e.g., Cr–Cr<sub>2</sub>Zr, Cr–Cr<sub>2</sub>Hf, Cr–Cr<sub>2</sub>Ta, Cr–Cr<sub>3</sub>Si, Ta–Cr<sub>2</sub>Ta and Ta–Ta<sub>5</sub>Si) were surveyed as potential materials for high temperature applications.

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Directional solidification of binary or pseudo-binary eutectics can produce well-aligned regular structures consisting of fibrous (rod-like) or lamellar constituents. Such structures may offer substantial increases in high-temperature strength, fracture properties, or creep resistance over those of conventionally cast alloys. Therefore, directionally solidified high-temperature eutectics are possible candidates for the eventual replacement of superalloys. We review here recent developments in the processing, microstructure, thermal stability and mechanical properties of directionally solidified eutectics.

## 2. Candidate eutectics for high temperature applications

A primary requirement for many high temperature structural applications is adequate oxidation resistance at temperatures above 1000°C. Therefore, attention has been focused on those alloys that have high concentrations of aluminum, chromium and silicon, since these elements have been shown to produce protective oxide scales of alumina, chromia, and silica, respectively [41]. To achieve useful strengths at temperatures of 1000–1600°C, melting points in excess of 1600°C are required. Most materials retain significant strength to approximately 0.5–0.6 of their absolute melting temperature,  $T_m$ . Using this criterion, Anton *et al.* [41] examined intermetallic compounds that have melting temperatures of 1600–2700°C, and concluded that materials based on the C14/C15 structure (Laves phase, e.g., Cr<sub>2</sub>Nb and Cr<sub>2</sub>Ta), A15 structure (e.g., Cr<sub>3</sub>Si and Nb<sub>3</sub>Al), D<sub>8</sub> structure (sigma phase, e.g., Ti<sub>5</sub>Si<sub>3</sub>), A12 structure ( $\alpha$ -Mn phase, e.g., Re<sub>3</sub>Nb) and Nb alloys are potential candidates for high temperature structural applications.

Table I lists several eutectic systems having melting points higher than 1600°C that have been studied recently as candidate materials. Some of these alloys have densities that are lower than those of currently used Ni-based superalloys (typically, around 8 g/cm<sup>3</sup> [42]), which gives them an advantage in aerospace applications, especially in rotating parts such as turbine blades or disks, where the strength to density ratio is important.

## 3. Microstructure morphology

The microstructures of binary eutectic alloys can exhibit a wide variety of geometrical arrangements of the two constituent phases. In general, the eutectic structure will exhibit a regular morphology (rod-like or lamellar) if both phases possess a low entropy of fusion, typically,  $\Delta S/R_g < 2$ , where  $\Delta S$  is the entropy of fusion and  $R_g$  is the gas constant [43]. The relative stabilities of the lamellar and rod-like structures have been discussed in detail by Jackson and Hunt [44] and Hillert [45]. When the volume fractions ( $V_f$ ) of the two eutectic phases are approximately the same ( $0.3 < V_f < 0.5$ ), which is encouraged by a phase diagram that is symmetrical about the eutectic composition, there is a preference for the formation of lamellar structures. An example is the Cr-Cr<sub>3</sub>Si eutectic in the Cr-Si phase diagram [46] shown in Fig. 1. The corresponding lamellar structure of this eutectic [15, 23, 24] is shown in Fig. 2.

When a pure eutectic alloy is constrained to grow unidirectionally, the two phases in the eutectic colonies grow cooperatively in a direction approximately parallel to the heat flow direction with the solid-liquid interface remaining planar throughout the solidification process. The resulting microstructure consists of alternating lamellae of the two eutectic phases. Usually, the microstructure of directionally solidified lamellar eutectics does not consist of perfectly parallel sheets of the alternating eutectic phases extending uninterrupted through the entire length of the material. As can be seen in Fig. 2a, discontinuous lamellae, which are referred to in the literature [47] as “terminations,” are evident on the transverse section. At most of these terminations, mismatch surfaces, or “faults,” separate two relatively perfect lamellar regions. Such lamellar faults [48] are common features of lamellar eutectics, with the terminations believed to provide conditions for the production of a constant interlamellar spacing at a particular growth rate [44, 49].

In the case of lamellar eutectic microstructures of a Cr-Cr<sub>3</sub>Si alloy (Fig. 2), the lamellar spacing is almost the same everywhere on the transverse sections (Fig. 2a), because they intersect the lamellae perpendicularly, but large differences can exist on the longitudinal sections (Fig. 2b), since such sections intersect

TABLE I Binary eutectics having melting points  $T_m > 1600^\circ\text{C}$  that have been recently investigated

Binary eutectic	Crystal structure	$T_E^b$ (°C)	$C_E^c$ (at.%)	Density of intermetallic <sup>d</sup>	Expected structure	Observed structure	Ref.
Cr-Cr <sub>3</sub> Si	A2-A15	1705	15.0 Si	6.5 g/cm <sup>3</sup>	Lamellar	Lamellar	[15, 24]
V-V <sub>3</sub> Si	A2-A15	1870	13.0 Si	5.7 g/cm <sup>3</sup>	Lamellar	Rod	[15]
Nb-Nb <sub>3</sub> Si <sup>a</sup>	A2-L1 <sub>2</sub>	1883	18.7 Si	7.3 g/cm <sup>3</sup>	Lamellar/rod	Lamellar/rod	[15]
Hf-Hf <sub>2</sub> Si <sup>a</sup>	A2-C16	2050	10.0 Si	11.7 g/cm <sup>3</sup>	Rod	—	—
Mo <sub>5</sub> Si <sub>3</sub> -MoSi <sub>2</sub>	D <sub>8m</sub> -C11 <sub>b</sub>	1900	54.0 Si	8.12-6.3 g/cm <sup>3</sup>	Lamellar	Lamellar	[80]
Cr-Cr <sub>2</sub> Ta <sup>a</sup>	A2-C14	1760	13.0 Si	11.2 g/cm <sup>3</sup>	Lamellar	Lamellar/rod	[81]
Cr-Cr <sub>2</sub> Hf <sup>a</sup>	A2-C14	1665	13.0 Hf	10.2 g/cm <sup>3</sup>	Lamellar	—	—
Cr-Cr <sub>2</sub> Nb <sup>a</sup>	A2-C14	1620	12.0 Nb	7.6 g/cm <sup>3</sup>	Lamellar/rod	—	—
Nb-Cr <sub>2</sub> Nb <sup>a</sup>	A2-C14	1650	50.0 Cr	7.6 g/cm <sup>3</sup>	Lamellar/rod	Lamellar	[12]
Ru-RuAl	A3-B2	1920	30.0 Al	8.3 g/cm <sup>3</sup>	Lamellar	Lamellar	[82]

<sup>a</sup>Intermetallic phase undergoes phase transformation during cooling.

<sup>b</sup> $T_E$ —Eutectic temperature.

<sup>c</sup> $C_E$ —Eutectic composition from phase diagram [46].

<sup>d</sup>All densities are from the ASTM Powder Diffraction File (PDF).

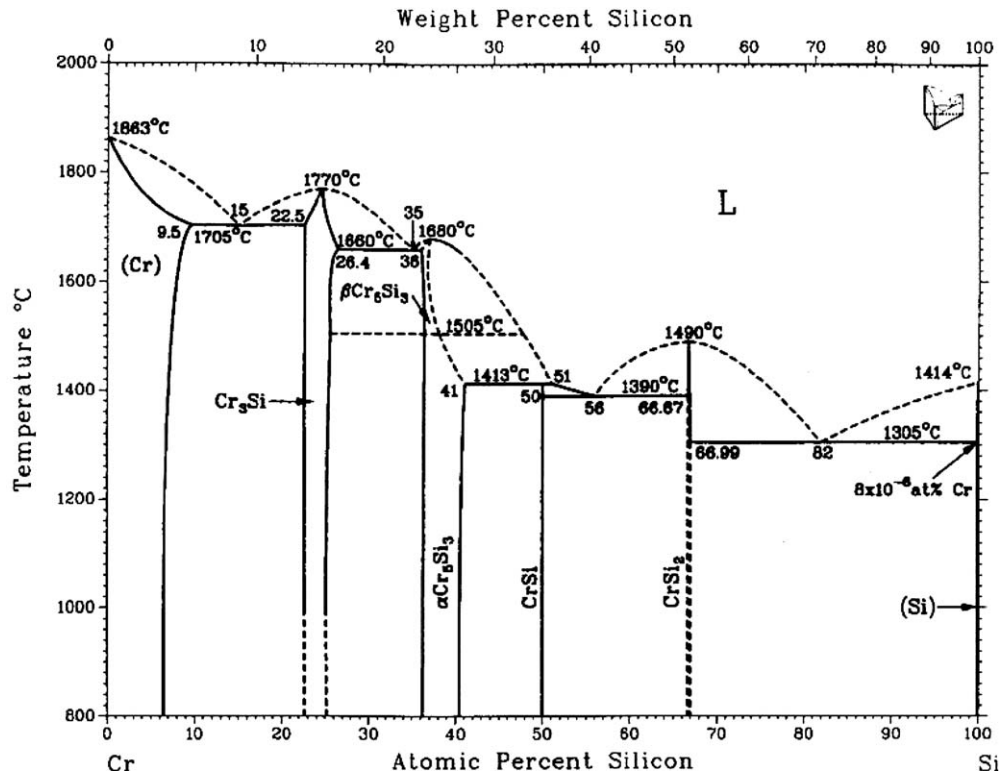


Figure 1 Binary Cr-Si phase diagram [46].

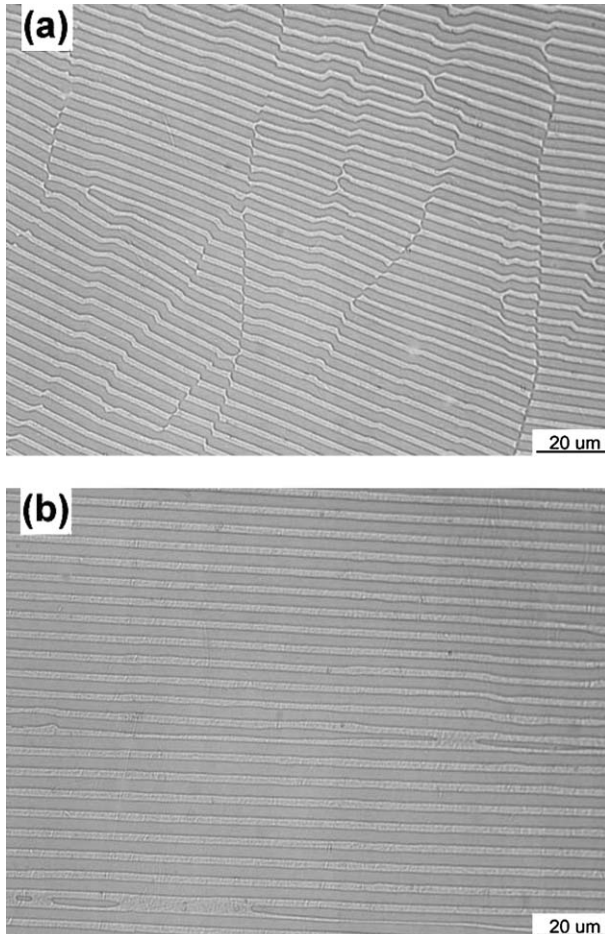


Figure 2 Optical micrographs showing lamellar microstructure of directionally solidified Cr-Cr<sub>3</sub>Si eutectic alloy: (a) transverse, and (b) longitudinal section (growth at 60 mm/h and 60 rpm). The thick and thin phases are Cr<sub>3</sub>Si and Cr-rich solid solution, respectively.

the lamellae at arbitrary angles leading to different projected widths of the lamellae. Measurements of lamellar spacing and thickness should therefore be made on sections that are transverse to the directional solidification direction and not on longitudinal sections.

The total interface energy is less for a rod-like morphology (compared to the lamellar morphology) if the difference in the volume fractions of the two phases is large (i.e., if one of the phases has  $V_f > 70\%$ ). In such cases, a rod-like structure is preferred with the major phase becoming the continuous matrix and the minor phase the discontinuous rods. An example of such an alloy is the NiAl-Mo ternary eutectic [50–56] in which the NiAl intermetallic compound is the continuous matrix and the Mo solid solution the rods (Fig. 3).

It is worth noting that volume fractions alone do not always determine whether the microstructure is rod-like or lamellar. Fig. 4 shows the rod-like structure of a V-V<sub>3</sub>Si eutectic alloy [15], where the V solid solution is the continuous matrix and the V<sub>3</sub>Si intermetallic the fibers. For reasons that are not entirely clear, the microstructure of this eutectic system is rod-like rather than lamellar even though it has near equal volume fractions of the two eutectic phases.

A fully eutectic structure, devoid of any cellular and dendritic regions, can be obtained not only in alloys having the exact eutectic composition but also at off-eutectic compositions if the growth conditions are carefully selected. This is of interest because it can be used to control the relative volume fractions of the phases and, therefore, the properties of the composite. In order to obtain eutectic-like structures in off-eutectic alloys one has to maintain a stable, planar solid-liquid interface during directional solidification. According to the

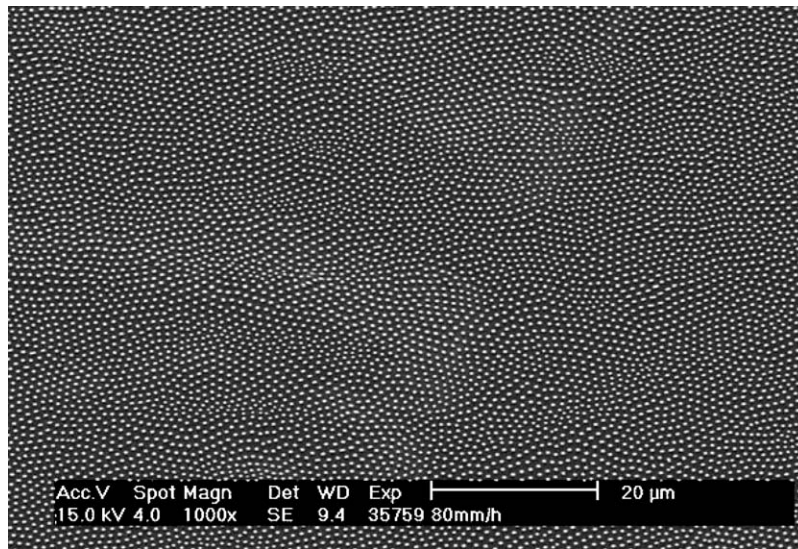


Figure 3 Cross-sectional SEM micrograph showing rod-like microstructure of directionally solidified NiAl-Mo eutectic alloy (growth at 80 mm/h and 60 rpm). The dark and bright phases are NiAl and Mo, respectively.

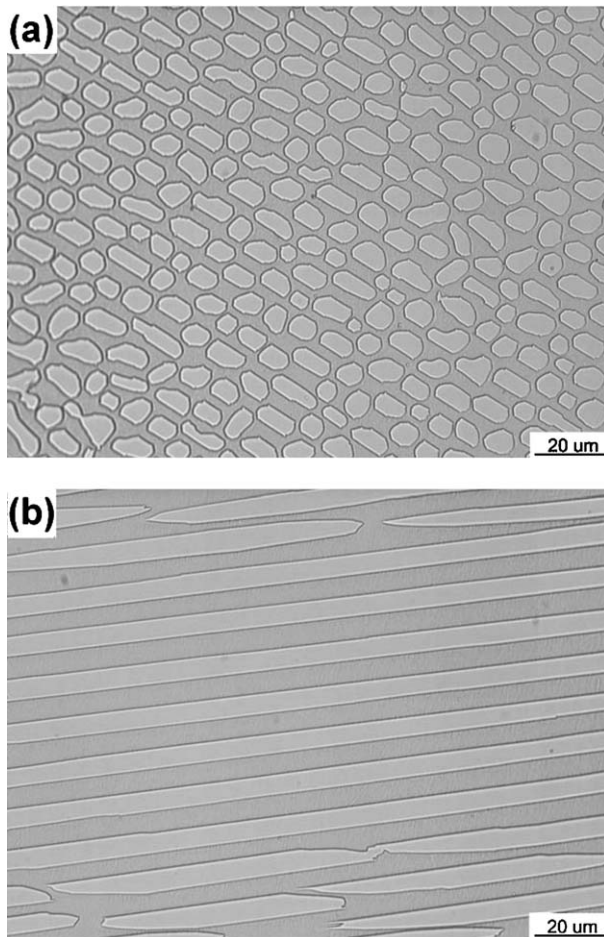


Figure 4 Optical micrograph showing rod-like microstructure of directionally solidified V-V<sub>3</sub>Si eutectic alloy: (a) transverse and (b) longitudinal section (growth at 20 mm/h and 60 rpm). The dark and light phases are V-rich solid solution and V<sub>3</sub>Si, respectively.

theory of constitutional supercooling, the growth condition for producing such an interface, in the absence of convection, is

$$\frac{G_L}{R} = \frac{-m_L(C_E - C_0)}{D} \quad (1)$$

where  $G_L$  is the temperature gradient in the liquid ahead of the interface,  $m_L$  is the slope of the liquidus,  $C_E$  is the eutectic composition,  $C_0$  is the initial composition of the solidifying alloy, and  $D$  is the solution diffusion coefficient [45, 57]. For a given alloy, the right hand side of Equation 1, which consists entirely of material parameters, is a constant. Similarly, for a given directional solidification system, the temperature gradient is a constant. Therefore, the only variable parameter is the growth rate,  $R$ , which has to be as slow as possible to favor a planar liquid-solid interface.

Using the above line of reasoning, fully eutectic microstructures (rod-like or lamellar) have been produced in Cr-Cr<sub>3</sub>Si off-eutectic alloys by directional solidification at slow growth rates [24]. At higher growth rates (at the same off-eutectic composition), dendritic regions appear within the lamellar microstructure. Depending on the composition and solidification condition, several microstructures, including lamellar, rodlike, cellular and dendritic plus lamellar can be obtained in the Cr-Cr<sub>3</sub>Si eutectic system, as indicated in the structure map shown in Fig. 5. The locations of the different

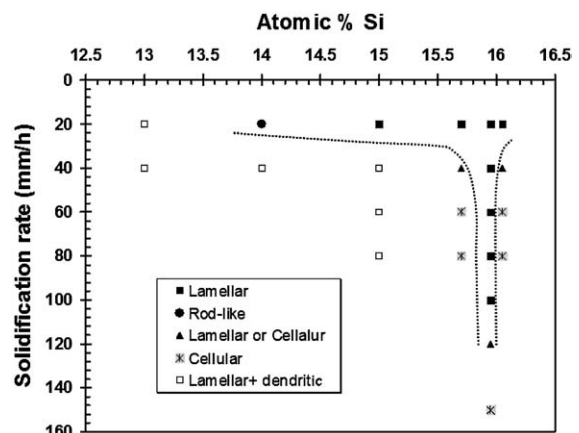


Figure 5 Structure selection map for various growth conditions and alloy compositions in Cr-Cr<sub>3</sub>Si alloys. The dotted line defines the region where eutectic-like structures (rod-like or lamellar) are obtained. All alloys grown at a rotation rate of 60 rpm [83].

regions in this map are consistent with the theory of coupled growth of eutectic alloys [58, 59].

#### 4. Effects of solidification parameters on interphase spacing

Regular eutectic growth depends on an interplay between the diffusion required for phase separation and the energy required for the formation of interphase boundaries. The interphase spacing is the result of a balance between two competing tendencies: on the one hand, to minimize the interphase spacing in order to shorten the diffusion path in the liquid near the interface, and on the other hand, to increase the spacing to minimize the interfacial area and hence the total interfacial energy. The most comprehensive treatment of this balance is that by Jackson and Hunt [44]. Under maximum growth velocity assumptions, they obtained the following relationship between growth rate  $R$  and interphase spacing  $\lambda$ , for both lamellar and rod-like eutectic structures:

$$\lambda^2 R = \text{constant} \quad (2)$$

where the constant is related to the magnitudes of the liquidus slopes at the eutectic temperature, the composition difference between the two phases, their volume fractions, the solid-liquid interface energies of two phases, and the liquid-solid interface shape.

The influence of solidification rates on the lamellar spacing has been investigated in detail for the Cr-Cr<sub>3</sub>Si system [24, 60]. It was found that the lamellar spacing  $\lambda$  varies linearly with the reciprocal of square root of growth rate  $R^{-1/2}$  for two different specimen rotation rates, 10 and 60 rpm (as shown in Fig. 6). It should be noted that the solidification rate cannot be used to vary the interphase spacing without limit because the well-aligned microstructure breaks down at very slow and very fast growth rates, being replaced with the so-called degenerate and cellular structures, respectively (see, for example, ref. [24, 60]). This dependence of lamellar spacing on growth rate is in agreement with the Jackson-Hunt theory [44]. Similar results have been observed also in the Ni-Ni<sub>3</sub>Si binary eutectic system [61],

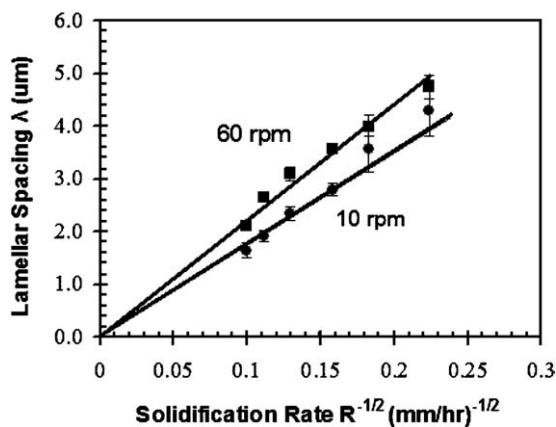


Figure 6 Effects of growth rate on lamellar spacings in directionally solidified Cr-Cr<sub>3</sub>Si eutectic alloys at fixed rotation rates of 10 rpm and 60 rpm [24].

although this eutectic system is not considered a candidate for high temperature applications because its melting point  $T_m$  is only about 1300°C. In the case of ternary eutectic systems, Rios *et al.* [62] have directionally solidified Nb-Al-Ni eutectic alloys ( $T_m = \sim 1550^\circ\text{C}$ ), and rod-like microstructures with three different phases (Al<sub>3</sub>Nb, Nb<sub>2</sub>Al and AlNbNi) were observed with the interphase spacing  $\lambda$  again decreasing with increasing solidification rate. A quantitative comparison of these experimental results with the Jackson-Hunt theory is difficult because precise knowledge of the surface energies and other physical parameters required to calculate the constants in Equation 1 is currently lacking.

The influence of fluid convection is not included in the Jackson-Hunt theory. However, there is usually forced convection in the molten zone during solidification, especially during directional solidification of materials with high melting points using the floating zone technique in which specimen rotation is employed to ensure uniform heating and homogeneous composition [39]. Limited theoretical analyses and experimental studies have shown that convective flow results in a change of the eutectic spacing during directional solidification. Quenisset *et al.* [63, 64] obtained a theoretical solution for the effect of convection on the eutectic spacing as follows:

$$\lambda^2 R = \frac{A}{1 - BG_u \lambda^2 / D} \quad (3)$$

where  $G_u$  is the gradient of flow velocity,  $A$  and  $B$  are constants, and  $D$  is the solution diffusion coefficient. Their analysis was for an ideal system in which the volume fractions of the two eutectic phases are the same, i.e.,  $V_f = 0.5$ . Baskaran and Wilcox [65] and Chandrasekhar *et al.* [66] extended the analysis for alloys in which the eutectic phases can have significantly different volume fractions and obtained the following result:

$$\frac{\lambda}{\lambda_0} = 1 + A' \varepsilon_0^2 \quad \text{for } V_f = 0.1-0.5 \quad (4)$$

where  $\lambda_0 = G_u \lambda_0^2 / D$ ,  $\lambda_0$  is the eutectic spacing without convection, and  $A'$  is a constant.

Because the gradient of flow velocity is proportional to the rotation speed [67], the above theoretical analyses predict that the interphase spacing increases with increasing rotation speed. This prediction has been verified in two eutectic systems, Cr-Cr<sub>3</sub>Si [24, 60] and Ti-Ti<sub>5</sub>Si<sub>3</sub> [39], by employing specimen rotation during directional solidification. A possible physical explanation of this effect is that convective flow produces a slight shift of the solute concentration field in the liquid near the liquid-solid interface, which tends to decrease the supercooling at the extreme condition of eutectic growth, thereby increasing the lamellar spacing [68].

#### 5. Thermal stability of microstructures

For high-temperature structural applications, the upper temperature limit is mostly dictated by microstructural

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TABLE II Crystallographic relationships for directionally solidified silicide eutectics

Eutectic	Orientation relationship	Ref.
Cr-Cr <sub>3</sub> Si	(111) <sub>Cr</sub> //(001) <sub>Cr<sub>3</sub>Si</sub> and (110) <sub>Cr</sub> //(210) <sub>Cr<sub>3</sub>Si</sub>	[15]
	(001) <sub>Cr</sub> //(001) <sub>Cr<sub>3</sub>Si</sub> and (110) <sub>Cr</sub> //(210) <sub>Cr<sub>3</sub>Si</sub>	
	(111) <sub>Cr</sub> //(001) <sub>Cr<sub>3</sub>Si</sub> and (123) <sub>Cr</sub> //(110) <sub>Cr<sub>3</sub>Si</sub>	[83]
V-V <sub>3</sub> Si	(111) <sub>V</sub> //(001) <sub>V<sub>3</sub>Si</sub> and (110) <sub>V</sub> //(∼4°)(210) <sub>V<sub>3</sub>Si</sub>	[15]
Nb-Nb <sub>3</sub> Si	(111) <sub>Nb</sub> //(111) <sub>Nb<sub>3</sub>Si</sub> and (110) <sub>Nb</sub> //(110) <sub>Nb<sub>3</sub>Si</sub>	[15]
	(111) <sub>Nb</sub> //(110) <sub>Nb<sub>3</sub>Si</sub> and (110) <sub>Cr</sub> //(101) <sub>Nb<sub>3</sub>Si</sub>	
Mo <sub>5</sub> Si <sub>3</sub> -Mo <sub>2</sub> Si	(110) <sub>MoSi<sub>2</sub></sub> //(110) <sub>Mo<sub>5</sub>Si<sub>3</sub></sub> and (002) <sub>MoSi<sub>2</sub></sub> //(220) <sub>Mo<sub>5</sub>Si<sub>3</sub></sub>	[80]

coarsening of the alloys. Since the directionally solidified intermetallic composites discussed in this review are being considered for such applications, it is important to consider their stability at elevated temperatures. When compared to arc-melted and drop-cast eutectic alloys, the microstructures of their directionally solidified counterparts tend to be much more stable. One possible reason is that directional solidification occurs very slowly—in hours rather than in seconds as is the case during drop casting—thereby giving time for the structure to approach equilibrium. In addition, during directional solidification, the total energy can be minimized if the two phases adopt low-energy orientation relationships relative to each other. Previous studies have shown that special orientation relationships do exist in most eutectic systems although the relationships may not be unique (Table II). In the Cr-Cr<sub>3</sub>Si eutectic system, for example, four different orientation relationships have been identified. In general the directions and planes tend to be low index. The special orientation relationships are expected to decrease the interfacial energy between the phases, thereby increasing the thermal stability of the eutectic structure.

Fig. 7 shows the coarsening behavior of a Cr-Cr<sub>3</sub>Si eutectic alloy after annealing at 1200°C. The lamellar structure of the drop-cast alloy (Fig. 7a) spheroidizes completely after a 120 h anneal (Fig. 7b). In contrast, no visible structural change was observed for a directionally solidified alloy even after much longer annealing times (e.g., 1728 h as shown in Fig. 7c) at the same temperature.

The driving force for this kind of microstructural coarsening and spheroidization is the decrease in the total interfacial energy, which is the product of the interfacial area and the unit interfacial energy. Lowering either parameter can slow down the coarsening kinetics. However, the former approach (i.e., make the lamellae or fibers thicker to start with) may compromise mechanical properties because for most materials strength and toughness are likely to be better when the structures are fine. Therefore, decreasing the unit interfacial energy becomes an important way to improve the thermal stability of the eutectic structure. This can be accomplished by microalloying with misfitting elements that segregate to the interphase boundaries and lower their energies.

In binary systems, there is an inverse correlation between solid solubility and grain boundary segregation

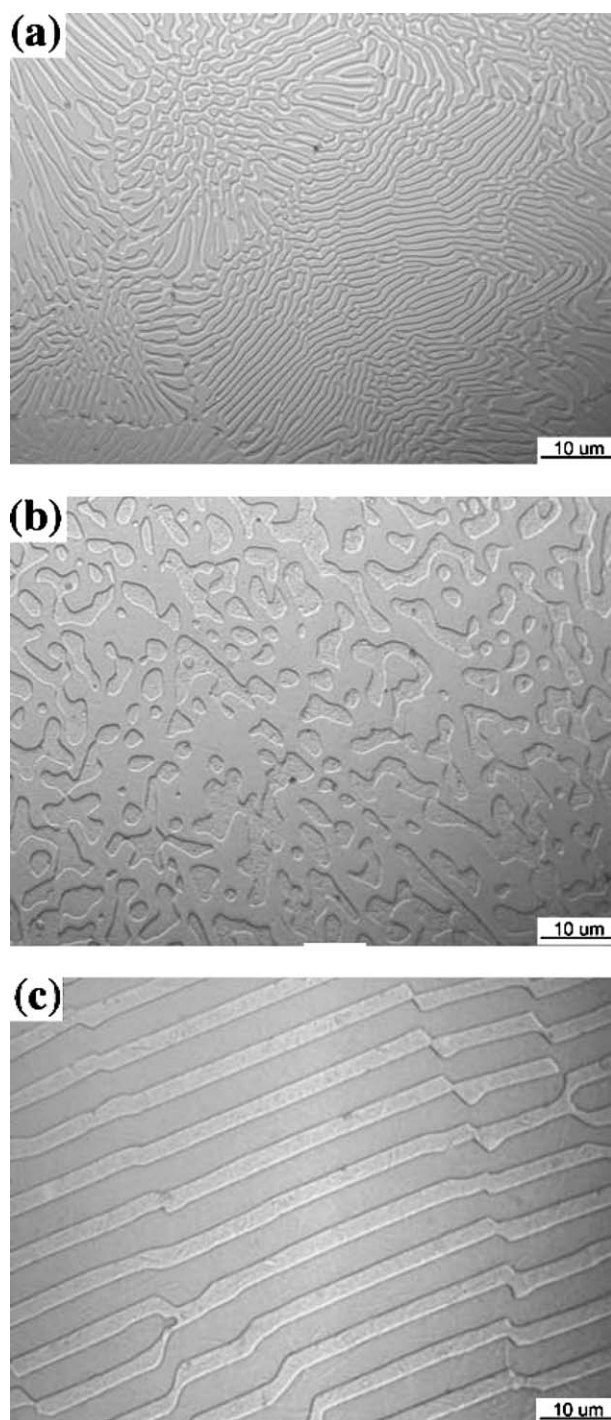


Figure 7 Optical micrographs showing coarsening behavior of the lamellar structure of Cr-Cr<sub>3</sub>Si alloy after annealing at 1200°C: (a) the lamellar structure of the drop cast alloy before annealing, (b) the structure of the drop cast alloy spheroidized completely after a 120 h anneal, and (c) no visible structure change for a directionally solidified alloy after 1728 h annealing.

potency [69, 70]. Solid solubility in turn decreases as the atomic size misfit between the solute and solvent increases (e.g., the Hume-Rothery rules preclude significant solid solubility when the size misfit exceeds 15%). Therefore, elements with large size misfits are expected to segregate strongly to grain boundaries [71]. Similar trends are expected to hold also for interfacial segregation in eutectic alloys. Limited experimental results [60] in the Cr-Cr<sub>3</sub>Si eutectic system confirm the above reasoning. It is found that the addition of very small

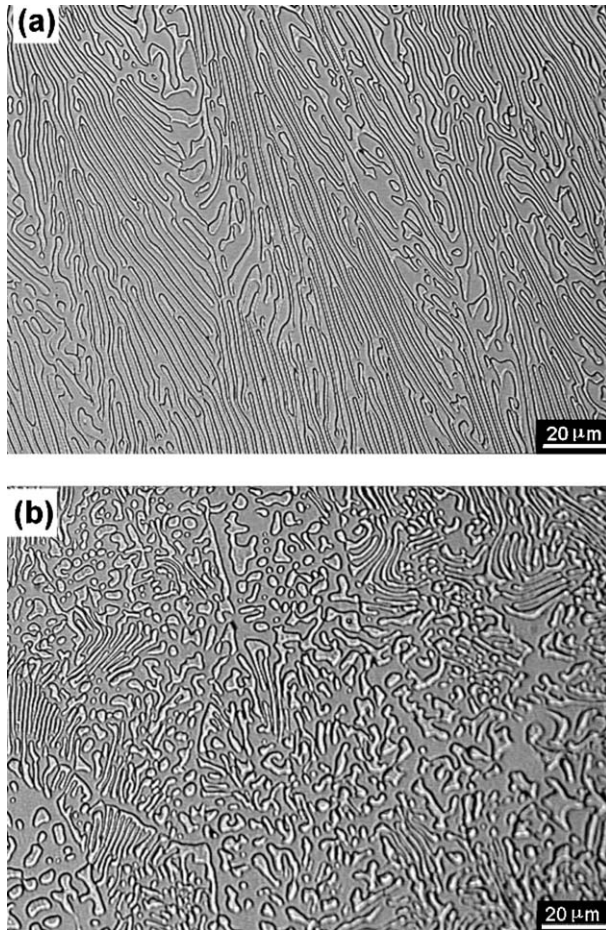


Figure 8 Effects of microalloying with (a) 0.01% Zr, and (b) 0.1% Ge on the microstructure of drop-cast Cr-Cr<sub>3</sub>Si lamellar eutectics annealed at 1200°C for 256 h [60].

amounts of alloying elements with large size misfits (e.g., Ce and Zr) slow down the coarsening kinetics significantly and improve the thermal stability of the lamellar eutectic structure (Fig. 8a). On the other hand, elements (e.g., Ge) that have similar sizes as the solvent atoms are less effective in slowing down the process of spheroidization (Fig. 8b).

In summary, directional solidification improves the thermal stability of the eutectic structure when compared to that produced by conventional casting. The stability can be further improved by adding very small amounts (“ppm levels”) of microalloying elements that segregate to the interphase boundaries and lower their energies.

## 6. Mechanical behavior

The mechanical behavior of conventional composite materials reinforced by relatively large wires or fibers ( $\sim 100 \mu\text{m}$  diameter) can be modeled by considering the load partitioned between the matrix and the reinforcing phases in proportion to their volume fractions. In contrast, the much finer microstructures ( $\sim 1 \mu\text{m}$ ) associated with *in situ* composites can lead to substantial additional, or indirect strengthening. This indirect strengthening has been explained with the help of continuum models and dislocation density effects (e.g., single dislocation-particle interaction models, multiple

TABLE III Hardness, Young's modulus, and brittle-ductile transition temperature of monolithic intermetallics with high melting points

Intermetallic	$T_m$ (°C)	Hardness (HV)	Modulus $E$ (GPa)	$T_{bd}^a$	Ref.
Cr <sub>3</sub> Si	1770	1200	351	>1200	[84]
V <sub>3</sub> Si	1870	1250	213	$\sim 1200$	[85, 86]
Mo <sub>3</sub> Si	2025	1285	300	1000	[87]
Mo <sub>2</sub> Si	2030	800	430	–	[87]
Mo <sub>5</sub> Si <sub>3</sub>	2180	1200	$\sim 300$	1250	[88]
Cr <sub>2</sub> Zr	1760	800	166	–	[89]
Cr <sub>2</sub> Ta	2020	–	175	–	[90]
Cr <sub>2</sub> Nb	1620	1000	218	–	[85]
RuAl	2060	310	267	–	[85]
Nb <sub>3</sub> Al	1960	910	–	$\sim 1000$	[91]

<sup>a</sup> $T_{bd}$ —Brittle-ductile transition temperature.

dislocation-particle interaction models and forest hardening models), as discussed in detail in ref. [25, 72].

Even without the additional strengthening effect of the composite, many intermetallic compounds by themselves offer high strength and good creep resistance at elevated temperature. Shah and Anton [73] evaluated refractory intermetallics with the A15 structure (e.g., Cr<sub>3</sub>Si) and found a significant (200°C) advantage over superalloys in terms of creep strength. Table III lists the microhardness and elastic modulus of several intermetallic compounds with high melting points. Most of these materials have very high hardness and elastic modulus, reflecting the strong interatomic bonding in these materials. Compression tests show that a relative high yield strength ( $\sim 700$  MPa) is achieved in a directionally solidified Mo-Mo<sub>5</sub>SiB<sub>2</sub> ( $T_2$ ) eutectic alloy at high temperature (1500°C) [74]. However, a major disadvantage is their intrinsic brittleness at room temperature. For example, the directionally solidified Mo-Mo<sub>5</sub>SiB<sub>2</sub> eutectic alloy has a fracture toughness of 11 MPa  $\sqrt{\text{m}}$  at room temperature, and below 1100°C this alloy does not show any ductility during compression testing [74]. Combining a brittle intermetallic phase with a ductile phase to produce “ductile-phase-toughened” *in situ* composites [19–24], therefore, has been the focus of attempts to improve the damage tolerance of high-temperature intermetallics at low temperatures. This contrasts with the approach in traditional metal matrix composites where the principal goal often is to enhance strength with the help of fiber reinforcements.

The results of three points bend tests show that the fracture toughness of single-phase V<sub>3</sub>Si can be significantly improved by incorporating a ductile V solid solution in the microstructure by directional solidification of V-V<sub>3</sub>Si eutectic alloys [75]. The fracture toughness of V-V<sub>3</sub>Si composites depends on their microstructure and interstitial impurity content. For eutectic composites containing nearly equal volume fractions of the continuous ductile V solid solution phase and discontinuous V<sub>3</sub>Si rods, fracture toughnesses of over 20 MPa  $\sqrt{\text{m}}$  have been reported, a significant increase when compared to that of the V<sub>3</sub>Si single phase ( $\sim 1.3$  MPa  $\sqrt{\text{m}}$ ). Similar improvements in fracture toughness have been realized in Nb-Nb<sub>5</sub>Si<sub>3</sub> *in situ* composites, where the ductile phase is (Nb) particles [76]. In the case of

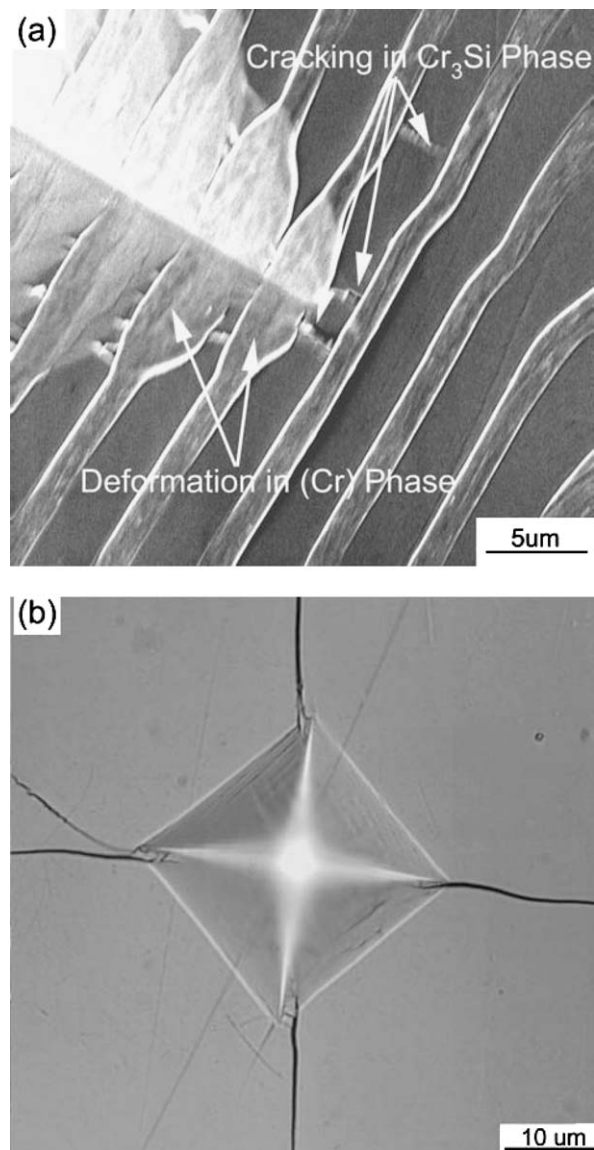


Figure 9 Micrographs showing: (a) cracks in Cr<sub>3</sub>Si lamellae stopped by the Cr-rich lamellae, and (b) cracks in the Cr<sub>3</sub>Si single crystal.

lamellar Cr-Cr<sub>3</sub>Si [24], although no fracture toughness values are currently available, microhardness testing showed that the brittle Cr<sub>3</sub>Si lamellae cracked whereas the more ductile Cr-rich lamellae deformed plastically and stopped the cracks that nucleated in the adjacent brittle lamellae (Fig. 9a). Therefore, the toughness of the Cr-Cr<sub>3</sub>Si lamellar structure is expected to be better than that of single phase Cr<sub>3</sub>Si where extensive cracking after indentation was observed (Fig. 9b).

In addition to interspersing ductile metal layers between the brittle intermetallic layers to enhance toughness, it is important also to improve the properties of the ductile phase itself. The use of body-center cubic metals as the ductile phase in many *in-situ* intermetallic composites (e.g., V, Cr, Nb and Hf in Table I) requires a better understanding of the factors contributing to the toughness of the ductile phase, including the role of interstitials and the effects of constraint on the evolution of stresses [77–79], if further improvements in toughness are to be realized. Additional work is also needed to improve the oxidation resistance of the bcc matrix in several of the intermetallic composites discussed in this review.

## 7. Summary

Directionally solidified intermetallic composites offer many advantages for high temperature structural applications, including high strength and excellent creep resistance at elevated temperatures. Their biggest drawback is poor ductility and low fracture toughness under ambient conditions. Limited progress has been made in improving the toughness of some eutectic systems. However, no binary system can currently satisfy all the property requirements for high temperature structural applications. Additional work is needed to identify and understand alloying effects on strength, toughness, creep resistance, microstructural stability and oxidation resistance.

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