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Inspection of the scientific literature reveals that intermetallic compounds have, in recent years, attracted considerable interest as a result of their unique elevated temperature characteristics. Among the wide range of intermetallic compounds that are actively being studied, MoSi₂ has been singled out as a result of its unique combination of properties, which include an excellent oxidation resistance, a high modulus of elasticity, and an elevated melting point (2030 °C). In view of this interest, the present work was undertaken with the objective of providing the reader with a comprehensive review of the mechanical and oxidation behaviour of MoSi₂, paying particular attention to the synergism between processing and microstructure. Accordingly, synthesis techniques, including powder metallurgy, self-propagating high-temperature synthesis, spray processing, solid-state displacement reactions, and exothermic dispersion, are critically reviewed and discussed. In addition, recent efforts aimed at using MoSi₂ as a matrix material in metal–matrix composites are also critically reviewed and discussed.

1. Introduction

Refractory metal silicides (e.g. MoSi₂, NbSi₂, TaSi₂ and WSi₂) are actively being used in a wide variety of applications, including very large scale integrated (VLSI) devices (as gate materials), interconnectors, ohmic contacts, heating elements and Schottky barriers, partly due to their excellent chemical and thermal stability and low electrical resistivity [1–5]. In recent years, molybdenum disilicide (MoSi₂) has attracted considerable attention [6–13] as an elevated-temperature structural material, as a result of its unique combination of physical characteristics. These include a moderate density of 6.31 g cm⁻³, a high melting point of approximately 2030 °C, an excellent oxidation resistance, and a high modulus at elevated temperatures. In view of these attributes, it is not surprising that MoSi₂ is considered to be one of the most promising candidate materials to be used in gas turbine engines expected to operate at temperatures of up to 1600 °C.

There are two critical requirements that must be satisfied in order for a structural material to be successfully utilized in elevated-temperature applications. Firstly, the material must possess attractive combinations of mechanical properties at the intended application temperature. Secondly, the oxidation resistance of the material must be sufficiently high to prevent environmental degradation during elevated temperature exposure.

In view of these requirements, the discussion that follows is divided into two parts. Firstly, recent findings on the deformation behaviour of MoSi₂ are succinctly reviewed, followed by a summary on the

measurement of the elastic properties of MoSi₂. Secondly, the environmental behaviour of MoSi₂ is discussed. Although MoSi₂ is inherently brittle at low temperatures, it exhibits plasticity at temperatures above the brittle–ductile transition temperature (BDTT, ~1000 °C). Accordingly, when MoSi₂ is deformed at temperatures below 1000 °C, fracture often occurs without significant plastic deformation [14–16]. Interestingly, however, despite this lack of plasticity, a significant amount of slip markings ($\{110\}\langle 3\bar{3}1\rangle$) near the fracture surface have been observed [15–17]. Moreover, in these studies, dislocations and stacking faults were reported to be active during elevated temperature deformation [16], thus rendering the deformation to be relatively ductile in nature, in contrast to that exhibited by most ceramic materials. At temperatures above 1200 °C, $\langle 100\rangle$ - and $\langle 110\rangle$ -type dislocations have been reported to control the plastic deformation [15–20]. In studies on the deformation behaviour of SiC_{whisker}-reinforced MoSi₂ metal–matrix composites (MMCs), it was reported that when tested at 1200 °C, no dislocation dissociation was observed in this material [17]. It was also suggested that the formation of stacking faults on $\{110\}$ planes further improves the high-temperature ductility [16]. The formation of stacking faults in MoSi₂ has been closely related to the phase stability of the C11_b tetragonal structure, relative to that of the C40 hexagonal structure [16].

The C11_b structure is a long-range ordered crystal structure made up by stacking three bcc lattices along the *c* axis, as depicted in Fig. 1. This particular crystal structure is thought to be responsible for the aniso-

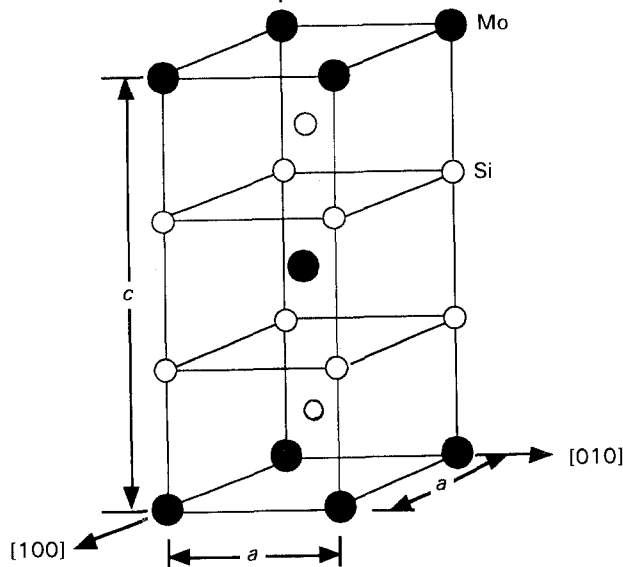


Figure 1 C11_b-type tetragonal unit cell structure of MoSi₂. $a = 0.3205$; $c = 0.7845$ nm [16].

trophy that is frequently associated with MoSi₂. For example, compression tests on MoSi₂ single crystals at elevated temperatures showed that the dominant primary slip planes are the {110} planes although slip on the {013} planes was also observed [14–20]. At approximately 1900 °C, MoSi₂ transforms from a tetragonal (C11_b type, $a = 0.3202$, $c = 0.7851$ nm) to a hexagonal (C40 type) crystal structure.

Regarding the measurement of the elastic properties of MoSi₂, some information is available. Nakamura and co-workers [18], for example, used a pulse echo method involving the measurement of elastic wave velocities in different orientations of MoSi₂ single crystals to determine the value of the elastic constants. Moreover, on the basis of this information, and using Voigt's, Reuss's, and Hill's approximations, Nakamura and co-workers [18] determined the magnitude of the bulk modulus, K , (209.7 GPa), Young's modulus, E , (439.7 GPa), shear modulus, G , (191.1 GPa), and Poisson's ratio, ν , (0.151) for polycrystalline MoSi₂.

Regarding environmental stability, MoSi₂ exhibits an excellent resistance to oxidation, equivalent to that of SiC. This is evidenced by the successful utilization of MoSi₂ as heating elements capable of operating in air, at temperatures in excess of 1500 °C [21–25]. In particular, the best grade of MoSi₂ heating element, commercially known as “Kanthal Super”, is capable of operating up to a temperature of 1800 °C. This material consists of a mixture of fine MoSi₂ particles bonded together with an aluminosilicate ($x\text{Al}_2\text{O}_3 \cdot y\text{SiO}_2$) glass phase [25]. The excellent oxidation resistance of MoSi₂ is attributed in part to the formation of a self-healing, glassy silica (SiO₂) layer, which prevents the MoSi₂ matrix from undergoing further oxidation. However, this low melting-point, glassy phase is detrimental to the elevated temperature strength. The formation of weak second phase or liquid phase

temperature exposure, and thus reduces creep resistance. In addition, the relative low elevated temperature strength of MoSi₂ further diminishes the creep resistance.

On the basis of the above findings, it is evident that despite its attractive combinations of elastic properties and oxidation resistance, MoSi₂ is inherently brittle when deformed at temperatures below 1000 °C, and furthermore exhibits a poor creep resistance at temperatures above 1200–1300 °C. Therefore, investigators have sought to achieve further improvements in low-temperature ductility and elevated temperature strength by blending MoSi₂ with a soft metallic phase (e.g. ductile phase reinforcement) and a hard ceramic phase (metal matrix composites), respectively [6–13, 26–53]. Despite encouraging preliminary results obtained with these two approaches, there are various issues that must be addressed before MoSi₂ may be successfully utilized as an elevated temperature structural material. In MMCs, for example, thermodynamic incompatibility between the MoSi₂ matrix and the ceramic reinforcements may ultimately degrade the oxidation resistance of MoSi₂. To that effect, the thermodynamic stability of MoSi₂ reinforced with various types of ceramic reinforcements has been studied extensively [9, 11, 30, 37, 40, 41, 43, 54–62] and will be discussed in a later section.

The objective of the present paper is to examine the various synthesis approaches that have been utilized in an attempt to improve the physical and mechanical behaviour of MoSi₂ and MoSi₂-based composites. Recent research results are emphasized, paying particular attention to key fundamental issues derived from novel synthesis approaches. We begin with a discussion of processing techniques, followed by recent findings on oxidation behaviour and mechanical properties. The paper concludes with a section on creep behaviour.

2. Processing techniques

A wide variety of processing techniques have been successfully utilized to synthesize MoSi₂ and the associated composites. In the following sections, these are critically discussed, paying particular attention to recent research findings. To discuss the results in a coherent manner, the present section has been subdivided into five subsections: powder metallurgy (PM) techniques, self-propagating high temperature synthesis (SPS), spray processing, solid-state displacement reactions, and exothermic dispersion (XDTM) techniques.

2.1. Powder metallurgy techniques

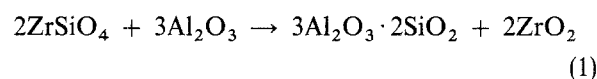
Powder metallurgy techniques typically involve the consolidation of discrete powders into a bulk form using temperature and/or pressure. Accordingly, the present discussion is divided into three sub-sections entitled: pressure-assisted sintering, reaction sintering, and mechanical alloying.

The pressure-assisted processing technique, including hot pressing, sinter forging, hot isostatic pressing (HIP), and hot extrusion, is an operation in which powder preforms are consolidated by applying pressure at elevated temperatures [63, 64]. A specific variation of this synthesis methodology, known as pressureless sintering, involves heating the powder preform in the absence of an external superimposed pressure. When applied to high-melting-point, high-strength materials, however, pressureless sintering is often time- and energy-intensive, and furthermore, often does not result in a fully dense product [63, 64]. In pressure-assisted processing, with the presence of a superimposed pressure, mechanisms such as grain rotation, grain boundary sliding, fragmentation, plastic deformation, and enhanced diffusion along grain boundaries all play a critical role in providing an enhanced densification rate which leads to reduced energy consumption, and often full densification [65–67]. Among the various pressure-assisted processing techniques, hot pressing and hot extrusion techniques typically involve heating the MoSi₂ powders in a die held under uniaxial pressure to densify or deform the material to a predetermined condition. In the case of sinter forging, the procedure is similar to that of hot pressing, but no lateral constraint is required. These three techniques, hot extrusion, hot pressing and sinter forging, are relatively easy and inexpensive to operate, but unfortunately they are severely limited in terms of their ability to produce complex shapes. Hot isostatic pressing, although more elaborate and costly to operate, provides advantages, such as no density variations, almost unlimited aspect ratio, uniform grain structure and the ability of achieving very complicated shape products, over the other three techniques [63, 64]. The modelling of pressure-assisted techniques has been aggressively pursued for several decades. Unfortunately, factors such as the variations in powder packing, varying particle morphologies, the influence of friction on deformation, and environmental effects have hindered the successful development of accurate models that may ultimately be applied to real processing situations [66–69].

Among the various pressure-assisted processing techniques that are available, hot pressing is most widely used. It has been successfully utilized to process monolithic MoSi₂ [7] and a wide variety of MoSi₂-based composites, such as those containing Nb- [31], W- [31], C- [32], ZrO₂- [43, 45], Al₂O₃- [46], SiC- [7, 34, 42], and TiC- [37] reinforced MoSi₂, with significant improvements in both flexure strength and fracture toughness. However, materials prepared by uniaxially hot-pressing a mixture of reinforcement and MoSi₂ powders are inherently simple in shape, and due to their poor machinability, often cannot be further processed into desired shapes. It is also evident, however, that further work is needed before pressure-assisted processing techniques may be commercially used to synthesize complex shapes of MoSi₂ and MoSi₂-based composites.

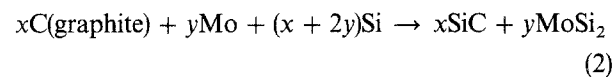
involve the *in situ* reaction of constituent powders, generally pressed into a preform, to produce a bulk composite preform that is different from the initial reactants [70]. Reactions can be either very fast (even explosive) or very sluggish, and either exothermic or endothermic, depending on starting and final reactant compositions, reactant compact microstructures; processing environments, and thermal boundary conditions [70]. In the discussion that follows, reaction sintering is defined as ‘reaction-assisted sintering’, which is diffusion-controlled and non-ignitable, and therefore is relatively sluggish. The high reaction rate processing techniques will be discussed in the SPS section.

Inspection of the available literature reveals that a wide variety of chemical reactions are generally involved in the preparation of structural materials using reaction techniques, ranging from powder synthesis (e.g., sol–gel technique, polymer pyrolysis, and decomposition of salts and organometallics) to direct production of a bulk material (e.g., chemical vapour deposition (CVD) and chemical vapour infiltration (CVI) techniques) [71]. However, as stated by Rice [70], although various reactions are capable of producing composite materials, of relevance are “reactions that can produce composite powders for consolidation into composites, or more commonly reactions involving a powder compact to form a composite product with the aid of heat, possibly with pressure as well, such as hot pressing, or hot isostatic pressing”. One well-known example, dating back to early 1980s, of the reaction synthesis approach involves the preparation of zirconia-toughened mullite (ZrO₂ + 3Al₂O₃·2SiO₂) by employing the following reaction [72]:



to form mullite–zirconia composites, which exhibited outstanding combination of mechanical properties.

Recently, Messner and Chiang [73–75] have successfully fabricated liquid-phase reaction-bonded SiC–MoSi₂ composites by using alloyed Si–Mo melts on the basis of the following reaction:



In this SiC–MoSi₂ composite, MoSi₂ is utilized as a reinforcement to toughen the SiC matrix. It is worth noting that the final SiC–MoSi₂ composite did not contain residual Si, whose presence is highly deleterious in elevated temperature applications. The liquid-phase reaction-bonding technique not only preserves the advantages of CVI, but also significantly reduces the time required for processing, and is capable of achieving a final density of 90%. However, it has been found [73] that below the melting of MoSi₂, mixtures of Mo and Si do not react completely, and a reaction layer develops, which inhibits further reaction.

On the basis of the previous findings [73, 74], Weiser *et al.* [76] employed pressureless reaction

SiC particulate were mixed with 10 vol % of elemental Mo and Si (an atomic ratio of 1:2), and then sintered in Ar at various temperatures. The addition of elemental Mo and Si was found to greatly enhance the densification of monolithic MoSi₂ at temperatures as low as 1400 °C. However, almost no densification was found in the composites containing SiC particulates, and this result was attributed to swelling and poor consolidation resulting from the undesirable reaction between SiC and Mo–Si elemental additives.

On the basis of the above-mentioned findings, and despite encouraging preliminary results, it is evident that the optimization of process parameters during reaction sintering requires further attention. However, even if the properties that are achieved with reaction sintered materials were only comparable with those of materials processed by conventional means, reaction sintering should potentially be the preferred approach in terms of production costs. Furthermore, it may be beneficial to use pressure-assisted processing techniques, combined with reaction sintering and liquid-phase sintering, e.g. Mo–Si reaction to form MoSi₂ and melting of Si, because this approach should provide a synergistic effect, not only to diminish the production costs, but also to improve mechanical behaviour.

2.1.3. Mechanical alloying

In recent years, the mechanical alloying (MA) technique, an application of mechano-chemistry, has attracted considerable interest [77–99]. MA involves repeated welding, fracturing and rewelding of powders (elemental or alloyed) during high-energy milling under a controlled atmosphere, as shown in Fig. 2 [77]. This process can be divided into four stages [96]:

- (i) first stage: an intense cold welding period;
- (ii) intermediate stage: a rapid fracturing period, forming lamellae;
- (iii) final stage: a moderate cold welding period, producing finer and more convoluted lamellae;
- (iv) completion stage: a steady state period.

Factors such as the amount of cold work, inter-layer spacing, and interstitial contamination critically influence the formation of compounds during MA [77]. During the high-energy milling process, repeated particle impact at contact points leads to a local concentration of energy, which under some circumstances may ignite a self-propagating reaction. This phenomenon, originally described by Atzmon [79–81] as “hot-spotting”, may lead to local melting and welding, enhanced inter-particle diffusion, chemical reaction, and ultimately to compound formation.

The mechanical alloying technique has been extensively utilized to produce a wide variety of compounds with highly refined microstructures [77–88]. Moreover, MA materials have been reported to exhibit non-equilibrium microstructural characteristics, such as the extension of solid solubilities [89, 90]. Not surprisingly, MA has been successfully used to combine alloying elements that would otherwise be unattainable by conventional techniques. One notable ex-

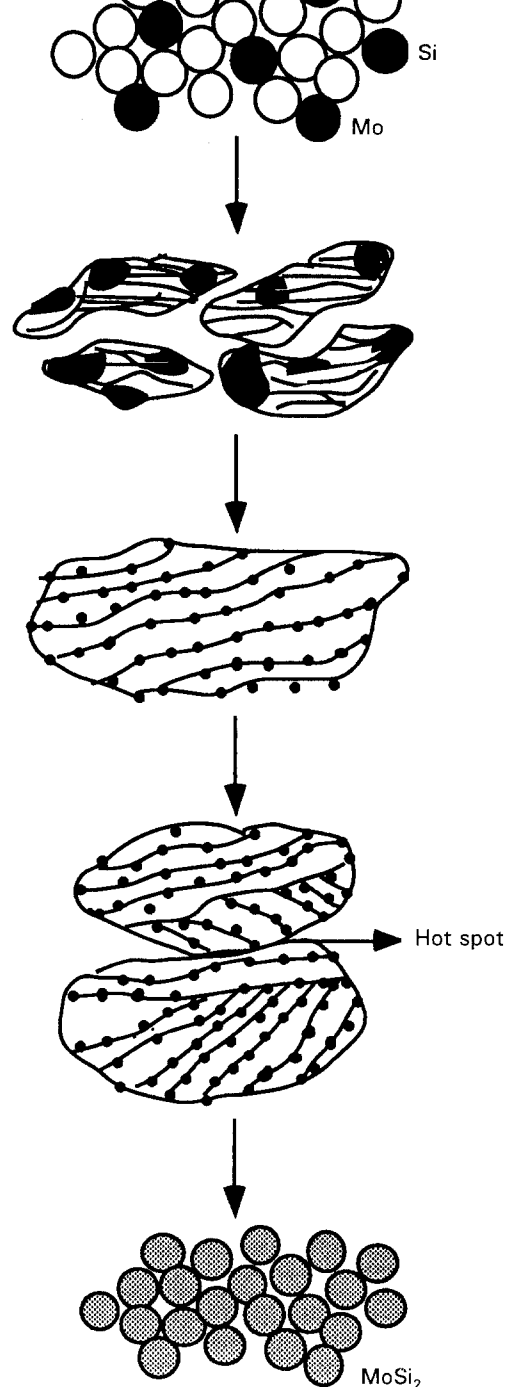


Figure 2 Schematic of MoSi₂ compound formation by mechanical alloying [77].

ample is superconducting intermetallic Nb₃Sn, which is difficult to prepare by conventional melting process, due to the significant melting point difference between Nb and Sn (~ 2240 °C) [91]. The large degree of microstructural refinement that is associated with MA materials often leads to dramatic improvements in mechanical behaviour. In 1966, for example, Seybolt [92] reported a 400% improvement in the rupture strength of MA Al₂O₃–FeAl relative to that of the matrix alloy.

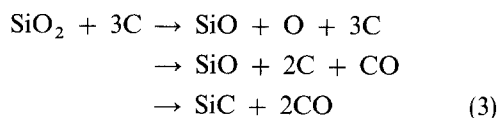
Some current applications of the MA include the production of oxide-dispersion strengthened alloys and intermetallic compounds [93, 94]; the development of oxidation and hot-corrosion resistant

systems (Fig. 15) [95], the production of superconducting and superconducting (Nb–Sn) materials [91]; and the preparation of amorphous compounds [78].

Recently, MA has been applied to the fabrication of silicides [77, 78, 86, 97, 98]. Accordingly, group V transition metal/Si silicides and amorphous Ti–Si alloy powders have been produced by mechanical alloying of elemental powders [78]. In group V transition metal/silicon systems, amorphization was reported in the Ta–Si system, but not in the Nb–Si system [96]. Factors such as the highly exothermic release of heat of mixing, fast interdiffusion rates, local melting, and the presence of a high defect concentration, have all been proposed to influence amorphization, although the precise mechanisms remain to be established [82].

The formation of MoSi₂ was first reported by Iwatomo & Uesaka [97], during MA of elemental Mo (5 μm) and Si (50 μm) powders. In this study, it was reported that α-MoSi₂, a low-temperature tetragonal phase, forms initially followed by the formation of a high-temperature hexagonal phase, normally present at temperatures in excess of 1900 °C. Following MA, the crystalline MoSi₂ particles were highly refined, exhibiting a grain size ranging from 5 to 10 nm. Moreover, Iwatomo & Uesaka [97] also confirmed the presence of amorphous regions in the MA MoSi₂ powder during prolonged milling time. The sintered MA MoSi₂ powders did not exhibit any significant differences in hardness or electrical conductivity when compared to equivalent material prepared using other techniques. However, the ultra-fine structure of the mechanically alloyed powders significantly reduced the sintering temperature (by nearly 400 °C), while yielding a final density in excess of 97% of theoretical [97]. Moreover, Ma *et al.* [98] reported that the formation of MoSi₂ by room-temperature high-energy ball milling of elemental powders is self-propagating.

Very recently, Jayashankar & Kaufman [99] used MA to synthesize *in-situ* SiC-reinforced MoSi₂ composites. In this work, Mo and Si powders, combined to yield the desired stoichiometry, were mixed with 4 wt % of C, followed by high-energy mechanical attrition. The overall reaction:



was proposed to describe the formation of SiC, and the simultaneous elimination of SiO₂ during hot pressing of mechanically alloyed MoSi₂ composite powders. The presence of C was found to significantly improve the overall homogeneity and cleanliness of the microstructure. Moreover, the significant weight loss noted in samples containing C was attributed to the formation of CO during MA, consistent with the results of Maloy *et al.* [32].

Schwarz *et al.* [100] recently reported a number of advantages that are available by using MA for the

formation of silicides: (i) higher hot-pressed density; (ii) lower hot-pressing temperatures for consolidation; (iii) better chemical homogeneity; (iv) improved room temperature hardness with second-phase additions. It is worth noting, however, that the formation of amorphous SiO₂ phase still occurred, although extreme care was taken during MA. In applications requiring creep resistance, it is imperative to produce MoSi₂ composites that are free of SiO₂. Hence, in principle, the MA technique may be successfully utilized to process MoSi₂ and MoSi₂ composites, as long as careful control of impurity content and environmental control are duly exercised.

2.2. Self-propagating high-temperature synthesis

Chemical reactions that are accompanied by the release of thermal energy are generally referred to as exothermic reactions. Self-propagating (or self-sustaining) high-temperature synthesis, so-called SPS (or SHS), is a technique involving the propagation of a high-temperature zone, driven by a highly exothermic reaction, through a compact of reactants. Although some of the reactions that were discussed are exothermic in nature, and hence in principle should be able to self-propagate, SPS generally proceeds at reaction rates that are substantially faster relative to those present during reaction sintering. The extent of reaction, η , is related to the temperature profile that is present during SPS, and may be represented by the following expression [101–103]:

$$\eta(x) = \frac{C_p \rho v (T - T_0) - \kappa_1 \frac{\partial T}{\partial x}}{(\kappa_2 - \kappa_1) \frac{\partial T}{\partial x} + q \rho v} \quad (4)$$

where C_p and ρ are the heat capacity and density of the product, respectively; v the velocity of combustion wave; T the reaction temperature; T_0 the initial temperature; κ_1 and κ_2 are the thermal conductivity of reactants and products, respectively; q is the heat of reaction; and x is the coordinate along which the combustion wave propagates.

Inspection of the available literature shows that SPS and other related techniques have been successfully used to produce a variety of alloys and composites [70, 104–118]. Early studies on transition-metal silicides prepared by SPS techniques showed that the reaction product contains one or more intermediate phases [104, 105]. In related work, Trambukis & Munir [106], and Bhattacharya [107] demonstrated that it is possible to use SPS to synthesize Ti₅Si₃ possessing attractive elevated temperature characteristics (e.g. strength and oxidation resistance) that are suitable for engineering applications. It has been found [106] that both heating rates and particle sizes critically influence the synthesis of silicides. In this study, SPS involved two reactions: a solid-state diffusion reaction for conditions of small particle size and low heating rates, and a liquid-state reaction for large particles and high heating rates. The time period

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