Available online at www.sciencedirect.com
ScienceDirect
Intermetallics 16 (2008) 758–768
Intermetallics
www.elsevier.com/locate/intermet

$MoSi_2$ laminate processed by tape casting: Microstructure and mechanical properties' investigation

S. Biamino*, A. Antonini, M. Pavese, P. Fino, C. Badini

Dipartimento di Scienza dei Materiali ed Ingegneria Chimica, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

Received 14 December 2007; received in revised form 12 February 2008; accepted 13 February 2008
Available online 11 April 2008

Abstract

In this investigation multilayered $MoSi_2$ was processed by tape casting, stacking of layers, debinding and pressureless sintering. The debinding treatment was optimized by means of thermogravimetric analysis and the effect of the sintering temperature on both microstructure and properties of the laminate was studied. The laminate microstructure was investigated and during sintering several phenomena were observed: reaction giving secondary phases (SiC and $Mo_{4.8}Si_3C_{0.6}$), reduction of silica contaminating the starting powders by carbonaceous residue left after debinding, coalescence of porosity and grain growth. Flexural and tensile strength, modulus, hardness and K_{Ic} were measured. The material behaviour in oxidising environment was assessed up to 1600 °C. The composite laminate showed enhanced strength and stiffness over monolithic $MoSi_2$. A toughening effect based on crack deviation was observed for $MoSi_2$ laminate. The material displayed self-passivating behaviour at high temperature and only limited oxidation in the temperature range where usually $MoSi_2$ suffers pesting.

Keywords: A. Molybdenum silicides; C. Sintering; F. Mechanical testing; G. Aero-engine components

1. Introduction

Today there is an increasing need for structural materials that can operate at temperatures getting progressively higher and higher and the promise of very strong tough structural materials at elevated temperatures has stimulated researchers for several decades. For example, advanced commercial and military aircraft engine and/or stationary gas turbine designs require materials that can withstand oxidising environments at temperatures above those attainable with conventional superalloys in order to improve performances as well as efficiency. In particular, for temperatures above 1200 °C, there are two general classes of materials available that show the potential to fulfil the required combination of oxidation, creep, fatigue and fracture toughness properties. These are structural ceramics such as Si_3N_4 and SiC and intermetallic compounds such as molybdenum silicides and niobium silicide-based alloys [1–7].

Actually, $MoSi_2$ is a promising intermetallic compound for high-temperature structural applications since it offers a combination of moderate density (6.23–6.3 g/cm^3 which is about 30% inferior to nickel-based superalloys), high melting point (2020–2030 °C), high thermal as well as electrical conductivity and excellent oxidation resistance at elevated temperatures [2,8,9]. Interestingly, $MoSi_2$ becomes ductile above 1000 °C (brittle-to-ductile transition temperature BDTT). This makes it more competitive with respect to silicon-based structural ceramics (Si_3N_4 and SiC), which are brittle from room temperature to high temperature [10]. In addition it is well recognized that $MoSi_2$ is an attractive wear-resistant material for applications at room and high temperature in corrosive and oxidative environments because of its high hardness (8 GPa) [11–13].

$MoSi_2$ is a dimorphic material: the tetragonal C11b-type α-$MoSi_2$ phase is stable up to 1900 °C; above this temperature α-$MoSi_2$ is transformed into the hexagonal C40-type β-$MoSi_2$ phase. This high-temperature phase (β-$MoSi_2$) melts in a congruent form at 2020 °C [8,9].

* Corresponding author. Tel.: +39 011 5644674; fax: +39 011 5644699.
E-mail address: sara.biamino@polito.it (S. Biamino).

0966-9795/$ - see front matter
doi:10.1016/j.intermet.2008.02.007

However, the application of $MoSi_2$ intermetallic compound is presently limited by its low fracture toughness at room temperature (2–3 MPa $m^{1/2}$), its poor tensile creep resistance at high temperature (>1300 °C) and its tendency to undergo ''pest oxidation'' through the formation and volatilization of MoO_3 within 400–600 °C [9,11–13].

There are some claims to have solved pest oxidation (which represents a problem not only for molybdenum silicides but also for niobium silicides) either by suitable alloying [14,15] or by microstructural control [16].

Its low toughness may partly result from the intrinsic difficulties of dislocation movement caused by special C11b crystal structure and the brittle grain boundary SiO_2 glass phase, which forms as a result of oxygen contamination of the powders during preparation process [17,18]. Therefore it is imperative to increase the room temperature fracture toughness and the high-temperature tensile creep resistance of monolithic $MoSi_2$ by means of proper toughening and strengthening. To this purpose, since the early 1970s, many researchers have been devoting their efforts to improve the mechanical properties of $MoSi_2$ by working in both material design and preparation techniques. The main approaches attempted to address the deficiencies in the mechanical properties of these materials include: (1) introduction of secondary phases (via reactions or artificially: ceramic particles, whiskers or continuous fibres); (2) tailoring of interfacial properties (in the case of artificially introduced secondary phases); (3) optimization of microstructure (grain size and morphology); and (4) alloying [2,3,9,10,13,19].

Several studies have been performed on the synthesis of $MoSi_2$ composites with different secondary phases such as Ta, Nb, W, ZrO_2, SiC, Si_3N_4, WSi_2, MoB, Mo_5Si_3, TiB_2, Al_2O_3, TiC, TiCN, AlN, La_2O_3, etc. and many relevant properties such as strength, toughness and high-temperature behaviour have been significantly improved [13,17,20–24]. At the same time, in order to eliminate the negative effects of the above-mentioned glassy SiO_2 phase, several methods have been adopted, such as HF washing, carbothermal or hydrogen reduction, aluminium addition, etc. [8,18,19,25–27].

Even though many processing routes have been evaluated for fabrication of $MoSi_2$ and its composites, the manufacturing of dense parts with a complex shape is still complicated today [28]. Usually manufacturing of dense parts without any glassy phase requires pressure assisted powder metallurgy techniques such as hot pressing or hot isostatic pressing, but also reaction bonding, combustion synthesis, infiltration and mechanical alloying techniques are under investigation [9,20,28–31].

An alternative method for enhancing toughness of ceramics is to pass from a monolithic structure to a multilayered one, generally processed by tape casting and sintering. The presence of ceramic layers with the same composition or a slightly different composition can activate a toughening mechanism, based on crack deviation phenomena, which increases the fracture energy through significant debonding of the interfaces. Such crack deviation phenomena are observed at the interfaces between the layers when weak interfacial bond exist (owing to the presence of residual porosity) [32–36] and/or according to the existence of residual stresses (related to differential sintering or differences in thermal expansion coefficient) [37–40]. Several multilayered ceramics have been investigated in the past [32–50]: the most widely studied materials are Al_2O_3 or Al_2O_3–ZrO_2 [36,40–43], SiC [32–34,44–48], and Si_3N_4 [49,50].

As regards $MoSi_2$-based multilayer, until now, only few works can be found in the literature. Shaw and Abbaschian [51] fabricated an SiC-whisker-reinforced $MoSi_2$ multilayer by tape casting and hot pressing. By hot pressing the multilayered structure disappears and the $MoSi_2$ increase in toughness is obtained according to the presence of SiC whiskers. On the other hand, to date, the employment of whiskers for composite preparation is not completely approved because of the problems with health protection that such type of material brings. Then it would be certainly preferable to achieve the increase in toughness exploiting the insertion of a secondary phase in the shape of the particles. There are two other possibilities to increase the toughness of $MoSi_2$ through the exploitation of a multilayered structure: the first one, concerns the realization of a sandwich structure, made of an $MoSi_2$ core and $MoSi_2 + 25$ vol.% Al_2O_3 external layers, by tape casting and hot pressing [52]; the second one is the preparation, by tape casting coupled to SHS, of a functionally graded material where the Al_2O_3 content in $MoSi_2$ progressively varies through the sample thickness [53].

For completeness sake some other works concerning the adoption of $MoSi_2$ as a secondary phase in multilayered ceramics can be mentioned. In the case of these materials $MoSi_2$ is used in order to improve the behaviour of other ceramics according to its intrinsic properties: Sciti and co-workers [54,55] prepared an AlN + SiC + $MoSi_2$ multilayer, where $MoSi_2$ is a minority phase (up to 30 vol.%) able to tailor electrical conductivity of the overall composite; Watanabe and co-workers [56,57] proposed an Al_2O_3/TiC/$MoSi_2 + Mo_2B_5$ multilayer, where $MoSi_2 + Mo_2B_5$ super-plastic layers are stacked in order to toughen Al_2O_3 at high temperature.

In this work the preparation of $MoSi_2$-based multilayer with increased mechanical properties has been investigated. The processing path involved tape casting, stacking of layers, debinding and pressureless sintering.

Since it is a common practice [8,18,26,27,31] to mix certain amounts of carbon into $MoSi_2$ powders in order to remove oxygen contamination, the processing path based on tape casting offers an alternative way for oxygen removal. In fact both binder and plasticizer leave a residual amount of carbon after the debinding process. The evolution of microstructure and chemical composition has been investigated starting from the green ceramic tapes and the debinded multilayered samples to finish with the sintered ones, which have been characterized with respect to their mechanical properties too.

2. Experimental

Multilayered $MoSi_2$ specimens were prepared based on our previous investigations about tape-casting technology [47,48]. The processing method involved several steps: slurry