PEST RESISTANT MOS₂-BASED MATERIALS CONTAINING IN-SITU GROWN β-Si₃N₄ WHISKERS

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Related U.S. Application Data

Division of application No. 09/500,497, filed on Feb. 9, 2000, now Pat. No. 6,288,000.

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ABSTRACT

A MoSi₂ pest resistant material includes in-situ grown β-Si₃N₄ whiskers. In addition to excellent pest resistance, the material provides a lower coefficient of thermal expansion for better match with continuous reinforcing fibers such as SiC fibers. A two stage heating and pressing production technique enables lower temperature processing with substantially full densification.

10 Claims, 2 Drawing Sheets
This application is a division of application Ser. No. 09/500,497, filed Feb. 9, 2000, now U.S. Pat. No. 6,288,000.

This invention was made with Government support under Contract No. NCC-3-637 by NASA. The Government has certain rights to the invention.

BACKGROUND OF THE INVENTION

The present invention relates to intermetallic materials based on MoSi₂, intermetallic matrix composites and methods of making the same. More particularly, the invention is directed to a MoSi₂ based material having an engineered microstructure provided through the use of in-situ reinforcement whiskers.

MoSi₂ is an attractive intermetallic for structural applications due to its excellent high-temperature oxidation resistance, low density and high thermal conductivity. However, it is brittle at low temperatures, weak at high temperatures and suffers from accelerated oxidation at intermediate temperatures. The accelerated oxidation of MoSi₂ at intermediate temperatures causes the material to disintegrate into powder, a phenomenon known as pesting.

Pesting is a general term describing the catastrophic oxidation of intermetallic materials at intermediate temperatures. The accelerated oxidation leads to the disintegration of the material and component failure. For MoSi₂, the temperature at which pesting is most pronounced is approximately 500°C. It has been observed that at 500°C bulk (i.e., non-composite) MoSi₂, as well as, composites of MoSi₂ with alumina and aluminum nitride also suffer total disintegration within relatively short time periods, e.g., 100 hours.

The pesting problem is detrimental to the use of MoSi₂ in high-temperature applications due to its excellent high-temperature oxidation resistance and its low-cost. However, pesting makes it unsuitable for use in high-temperature environments.

The accelerated oxidation of MoSi₂ at intermediate temperatures appears to result in matrix cracking during fabrication and severe matrix cracking during thermal cycling which in turn results in component failure. Possible reinforcing fibers include high strength ceramic fibers such as silicon carbide, single crystal alumina, and ducitle, high strength molybdenum and tungsten alloy fibers. Ductile niobium fibers have shown improvements in low temperatures strength and toughness, but a severe reaction between the fiber and MoSi₂ limits its use and, in any case, it does not provide improved high-temperature characteristics. The addition of silicon carbide whiskers has yielded improvements in room temperature toughness, but pesting and coefficient of thermal expansion mismatch continue to be problems.

SUMMARY OF THE INVENTION

It has now been discovered that a MoSi₂ based material may be provided with an engineered microstructure through processing and composition control. In-situ reinforcement of whisker type β-Si₃N₄ grains in a MoSi₂ matrix offers a unique combination of attributes. The in-situ reinforcement is believed to provide a more tortuous crack path with elongated grains or whiskers which lead to crack bridging and deflection resulting in very high fracture toughness.

The invention contemplates a new MoSi₂ based alloy composition which exhibits excellent pest resistance at low temperatures (400 to 600°C), good coefficient of thermal expansion match with potential fiber reinforcement, excellent oxidation resistance at elevated temperatures and high fracture toughness enabling its use as a monolithic material. Accordingly, a MoSi₂-based matrix contains a high-volume fraction of randomly oriented in-situ grown long whisker type grains of β-Si₃N₄ in the MoSi₂ matrix. The matrix is characterized in part by a toughened microstructure, lower density, lower coefficient of thermal expansion, excellent resistance to pest attack, and it is much stronger than the binary MoSi₂ material.

The invention also contemplates processing conditions to achieve fully dense alloys with engineered microstructure through the use of sintering aids to grow the long whiskers of β-Si₃N₄ in the matrix. During processing, high-temperature and pressure conditions are used to convert the α-Si₃N₄ particles to randomly oriented β-Si₃N₄ long whiskers. Suitable sintering aids include rare earth oxides.

It is presently believed that the improved pesting is related to the formation of more protective silicon oxynitride, Si₃N₄Oₓ, and/or mullite/SiO₂ oxide scales that suppress the formation of non-protective MoO₃. The invention also contemplates forming an outer protective layer of Al₂O₃-SiO₂ followed by an inner layer of SiO₂ for better oxidation resistance in reducing or low partial pressure oxygen atmospheres.

The invention also contemplates the use of the MoSi₂-β-Si₃N₄ as a matrix in a ceramic fiber reinforced composite to achieve high specific strength, high first matrix cracking stressed and toughness without exhibiting any pesting or cracking during long-term thermal cycling at high and low temperatures. Silicon carbide fibers comprise a preferred reinforcing fiber.

According to a first preferred composition of the invention, there’s provided MoSi₂ based matrix materials containing at least about 20 percent by volume β-Si₃N₄ whisker type grains based on the combined volume of the MoSi₂ and the β-Si₃N₄. More preferably, the composition of the invention comprises from about 30 to about 50 percent by volume β-Si₃N₄ based on the combined volume of the MoSi₂ and β-Si₃N₄.
The achievement of the whisker type β-Si₃N₄ grains is enhanced by the use of rare earth oxide sintering aids. The rare earth oxides are nano sized. Preferred rare earth oxides include Y₂O₃ and Al₂O₃. The sintering aids are used in amounts ranging from 2 to 6 percent by weight based on the combined weight of the MoSi₂ and β-Si₃N₄.

A preferred fiber reinforced composite comprises the above noted MoSi₂-βSi₃N₄ composition as a matrix material and ceramic reinforcing fiber. The reinforcing fiber is interspersed with the matrix material. The matrix material comprises at least about 50 percent, and more preferably about 70 percent by volume of the composite based on the combined volume of the matrix material and the β-Si₃N₄ reinforcing fiber. In more preferred arrangements, the reinforcing fiber is a silicon carbide fiber, and it is present in the matrix in an amount of about 30 percent by volume based on the combined volume of the matrix and the reinforcing fiber.

In accordance with the method of the present invention and preferred processing, mixtures of MoSi₂ and Si₃N₄ are blended and milled to micrometer particle size with the prior addition of sintering aids. The mixtures are formed into thin sheets or plates using vacuum hot pressing to achieve a relatively high green density. This first stage is followed by hot isostatic pressing to achieve full density as well as growth of whisker type grains of β-Si₃N₄. This two stage processing with the use of sintering aids enables reduction of the maximum heating temperature without reduction of the final level of densification.

BRIEF DESCRIPTION OF THE DRAWINGS
FIG. 1 is a SEM-BSE image showing the long whisker type β-Si₃N₄ grains randomly distributed in a MoSi₂ matrix;
FIG. 2 is a plot showing the flexural strength at various temperatures for MoSi₂-βSi₃N₄ and AS-800;
FIG. 3 is a graphical comparison of the electrical conductivity of various materials; and
FIG. 4 is a plot showing the reduced coefficient of thermal expansion for MoSi₂ compounds with in-situ β-Si₃N₄ whiskers.

DETAILED DESCRIPTION OF THE INVENTION
The in-situ reinforced MoSi₂-βSi₃N₄ yields a highly developed microstructure characterized by desirable physical properties. The in-situ reinforced materials have a lower density (4.5 g/cc) than nickel or cobalt based superalloys (about 8.5 g/cc). In addition, higher fracture toughness (about 20 MPa(m)½) and impact resistance at room and operating temperatures as compared with SiC/SiC. The in-situ reinforced alloys also provide improved damage tolerance, reliability and creep resistance as compared with SiC/SiC. Also, higher thermal and electrical conductivities are achieved than with SiC/SiC. As noted above, the in-situ reinforced materials also enable low cost EDM and laser machining. It should be appreciated that the SiC/SiC materials are more costly since they employ fibers and coatings.

In accordance with the invention, mixtures of MoSi₂ and Si₃N₄ are blended and milled to obtain an average particle size of less than about two micrometers in diameter. The mixtures are then consolidated into thin sheets or plates using vacuum hot pressing to achieve a relatively high density, e.g., 90 percent green density. Full density as well as growth of whisker type grains of β-Si₃N₄ are achieved with hot isostatic pressing. In this manner, the α-Si₃N₄ particles are transformed into β-Si₃N₄ as randomly oriented long whiskers that are well dispersed in the MoSi₂ matrix.

EXAMPLE 1
MoSi₂ based alloys consisting essentially in amounts by volume percent of about 30 to 50 percent Si₃N₄ having a particle size of one to two microns were prepared in the following manner. The Si₃N₄ obtained from UBE Inc. was ground in a Union Process Model 1-S attritor mill for about eight hours using WC grinding media. The grinding media had a diameter of about six mm, and a ball to powder ratio of 20 was used to reduce about 95 percent of the particles to a size of less than two microns.

MoSi₂ powder having at least 98.5 percent purity and a −325 mesh size was obtained from Johnson Matthey Inc. (Aesar Inc.). The MoSi₂ powder was combined with the ground Si₃N₄ and about 2–6% by weight sintering aids. The sintering aids were nano size rare earth oxides such as Y₂O₃ and Al₂O₃ obtained from Nanotek Inc.

Three batches of about 530 grams each were prepared as described above, and combined in a SiC jar mill containing about 1500 grams of silicon carbide grinding media in the form of six mm diameter balls. The combined batches were milled for about 24 hours.

The combined batches were then further milled in the Union Process Model Research 1-S attritor with an impeller rotation speed out 450 rpm for eight hours using six mm diameter WC grinding media. The ball to powder ratio was 20:1. The outer jacket of the attritor was cooled with flowing liquid nitrogen to promote efficient grinding. After eight hours of milling, the powder was separated anaerobically from the grinding media in a glovebox containing an argon atmosphere. The resulting powder mixture had an average mean particle size of 1.25±0.71 micrometers at 99 percent confidence.

The powder mixture was consolidated into a 12 cm long by 5 cm wide by 0.3 cm thick plate by vacuum hot pressing at 1600°C and 128 MPa or 1800°C and 84 MPa for four hours to achieve more than 90 percent green density. The hot pressed plate was enclosed in a tantalum hot isostatic press (HIP) canister together with a silicon carbide back-up plate. The HIP canister was sealed using electron beam welding. Further consolidation of the hot pressed plate was achieved by hot isostatic pressing between 1800–1900°C and 300 MPa for two hours. During hot isostatic pressing, full densification as well as growth of whisker type grains of β-Si₃N₄ were achieved. The use on the sintering aids and the two-step consolidation process enabled the use of lower temperatures then could be used if hot pressing were done alone for purposes of growing β-Si₃N₄ grains. (e.g. if hot pressing alone were used, the required temperature would be in the range of 2000–2100°C at 126 MPa for four hours.) This resulted in fully dense and β-Si₃N₄ grain microstructure as shown in FIG. 1. The α-Si₃N₄ particles are transformed into β-Si₃N₄ as randomly oriented long whiskers that are well dispersed in the MoSi₂ matrix. The β-Si₃N₄ whiskers appear to be quite stable, with very little or no reaction with the MoSi₂ even at 1900°C. In some isolated areas the MoSi₂ phase was detected. This is believed to be due to the lack of stoichiometry in commercially available MoSi₂.

The fracture toughness of the materials in accordance with Example 1 was measured at room temperature by preparing ASTM chevron notched bend specimens. For purposes of testing, a second duplicate batch of materials was prepared and the samples are referred to below as being of batch 1 or batch 2. The fracture testing was done at room temperature using an Instron test machine fitted with a four point bend fixture.
From the load displacement data and specimen dimensions, the valid $K_{IC}$ was calculated using a slice finite element model. The slice model is based on the relationship:

\[
K_{IC} = \frac{(P_S - S_i)W}{(W^2/2)}
\]

Where $K_{IC}$ is the fracture toughness in MPa(m)^{0.5}, $P$ is the load at break in MPa, $S_i$ and $S_f$ define the gripped sample span, $F$ is a sample geometry constant, $B$ is the sample thickness in mm, and $W$ is the sample width in mm.

### TABLE 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>B (mm)</th>
<th>W (mm)</th>
<th>$\alpha_{II}$</th>
<th>$\beta_{II}$</th>
<th>$\gamma^*$</th>
<th>P (N)</th>
<th>$K_{IC}$ (MPa (m)^{0.5})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch I</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MS-1</td>
<td>3</td>
<td>6</td>
<td>1.2</td>
<td>4.8</td>
<td>3.2</td>
<td>270.5</td>
<td>17.0</td>
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<tr>
<td>MS-2</td>
<td>3</td>
<td>6</td>
<td>1.2</td>
<td>4.8</td>
<td>3.2</td>
<td>270.5</td>
<td>17.0</td>
</tr>
<tr>
<td>MS-3</td>
<td>3</td>
<td>6</td>
<td>1.2</td>
<td>4.8</td>
<td>3.2</td>
<td>270.5</td>
<td>17.0</td>
</tr>
</tbody>
</table>

**MATERIAL ID:** MoSi$_2$-Si$_3$N$_4$, MS-1, MS-2, MS-3

**TEST TEMP.: ROOM TEMP.**

**CROSS HEAD SPEED:** 8.5 x 10^{-5} s^{-1}

**FOSSIL’S RATIO:** 0.32

The average $K_{IC}$ of this material was about 17 MPa(m)^{0.5}. The room temperature fracture toughness of MoSi$_2$-Si$_3$N$_4$ without the whiskers of $\beta$-Si$_3$N$_4$ was about 5.0 MPa(m)^{0.5}. Accordingly, the $\beta$-Si$_3$N$_4$ whiskers improved the fracture toughness by more than a factor of three as compared with the Si$_3$N$_4$ particulate in MoSi$_2$.

The in-situ Si$_3$N$_4$ toughened MoSi$_2$ has a higher fracture toughness than commercially available in-situ toughened Si$_3$N$_4$. For example, AS-800 has a fracture toughness of about 8.5 MPa(m)^{0.5} and NKK has a fracture toughness of about 10 MPa(m)^{0.5}. The higher fracture toughness of MoSi$_2$-$\beta$-Si$_3$N$_4$ as compared to in-situ toughened Si$_3$N$_4$ is believed to be derived from the combined effects of efficient crack bridging and grain pull-out lead to a rising crack growth resistance curve (R-curve behavior) as confirmed by the testing of this material using the indentation crack size, indentation-strength method, SEPB and chevron notched bend method as indicated by the data of Table 1. A consequence of this R-curve is that this material will have a higher Weibull modulus.

The flexural strength of the material of Example 1 was measured using ASTM standard specimens (3 mm thick by 6 mm wide by 50 mm long MOR bars) of MoSi$_2$-$\beta$-Si$_3$N$_4$ at various temperatures between room temperature and 1400°C in air. FIG. 2 shows the flexural strength of MoSi$_2$-$\beta$-Si$_3$N$_4$, MoSi$_2$-$\alpha$-Si$_3$N$_4$ and AS-800 as a function of temperature. FIG. 2 clearly indicates that the strength of AS-800 is superior to MoSi$_2$-$\beta$-Si$_3$N$_4$ at all temperatures. Also, the strength of MoSi$_2$-$\beta$-Si$_3$N$_4$ is higher than MoSi$_2$-$\alpha$-Si$_3$N$_4$. As an intermetallic compound, the MoSi$_2$ offers significant potential for further improving the strength by solid solution alloying.
The composite of claim 7, wherein said matrix material comprises at least 20% by volume whiskers of $\beta$-$\text{Si}_3\text{N}_4$ based on the combined volume of said molybdenum disilicide and whiskers of $\beta$-$\text{Si}_3\text{N}_4$.

The composite of claim 7, wherein said ceramic reinforcing material comprises silicon carbide fibers.
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page, Item [54] and Column 1, line 1,
Please delete “MOSI₂-BASED” and insert therefor -- MoSi₂-BASED --.
Line 3, please delete “β-Si₃N₄” and insert therefor -- β-Si₃N₄ --.

Column 2,
Line 64, please delete “compositionof” and insert therefor -- composition of --.

Column 5,
Line 11, please delete “Y is a” and insert therefor -- Y is a --.

Signed and Sealed this
Twenty-third Day of July, 2002

Attest:
JAMES E. ROGAN
Attesting Officer
Director of the United States Patent and Trademark Office