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Investigation of dynamic Young's modulus for molybdenum disilicide–titanium trisilicide ($MoSi_2$–Ti_5Si_3)

A. WOLFENDEN, K. J. BAUER
Advanced Materials Laboratory, Mechanical Engineering Department, Texas A&M University, College Station, TX 77843-3123, USA
J. J. PETROVIC
Los Alamos National Laboratory, Los Alamos, NM 87545, USA

Molybdenum disilicide–titanium trisilicide ($MoSi_2$–Ti_5Si_3) is a ceramic matrix composite (CMC) created for the purpose of improving the mechanical properties of molybdenum disilicide. Five alloys of this CMC were prepared by varying the ratio of volume per cent Ti_5Si_3 to volume per cent $MoSi_2$. Evaluation of the specimens using the piezoelectric ultrasonic composite oscillator technique (PUCOT) determined the values of Young's modulus to range from 303 to 378 GPa at room temperature increasing with volume fraction of $MoSi_2$. The values of Young's modulus for temperatures up to about 400 °C for each alloy decrease linearly with respect to increasing temperature. Damping within the specimens is independent of strain amplitude at room temperature, but shows some strain amplitude dependence at higher temperatures. The values of density for the alloys, determined using Archimedes' method, range from about 5200 to 5900 kg m^{-3}, and compare favourably with the values determined by the rule of mixtures.

1. Introduction

Molybdenum disilicide ($MoSi_2$) is an intermetallic compound known for its excellent high temperature oxidation resistance and high melting point (2030 °C), with brittle-to-ductile transition at 900–1000 °C [1, 2] and a body centred tetragonal *tI*6 (*c* 1 1 *b*) structure [3]. It is desirable to lower the brittle-to-ductile transition temperature, increase low temperature fracture toughness and improve both thermal shock/fatigue resistance and elevated temperature strength/creep resistance, while retaining good oxidation resistance at high and intermediate temperatures [2]. Articles [1, 2] suggest these mechanical property improvements are obtainable through $MoSi_2$ composites, with several composites suggested.

This investigation considers the ceramic matrix composite molybdenum disilicide–titanium trisilicide ($MoSi_2$–Ti_5Si_3), with emphasis on measurement of dynamic Young's modulus at elevated temperatures up to about 400 °C. Concurrent property findings of mass density, strain amplitude dependence of damping and activation energy are also presented.

2. Experimental procedure

The specimens were prepared at the Los Alamos National Laboratory (LANL) with the following ratios of volume per cent Ti_5Si_3 to volume per cent $MoSi_2$: 10:90, 20:80, 30:70, 40:60 and 50:50. Cerac-325 mesh Ti_5Si_3 and Alfa-325 mesh $MoSi_2$ powders were mechanically blended in the proper amounts and consolidated by hot pressing at a maximum temperature of 1850 °C. Two specimens of each alloy were then prepared, each measuring approximately 1.5 × 2.0 × 25 mm.

Determination of dynamic Young's modulus (the ratio of stress/strain in the elastic regime) was accomplished using PUCOT [4–6]. Preliminary requirements to the PUCOT application include determination of exact specimen length, mass density and resonant frequency. The mass densities were easily obtained by Archimedes' method. The resonant frequencies were estimated by assuming a value for Young's modulus and solving for resonant conditions. The range of specimen frequencies was compared to the frequency of available quartz crystals, and crystals capable of satisfactorily testing all specimens were chosen. Each specimen was evaluated at room temperature using PUCOT. Invalid test results led to slight adjustments in specimen length, while a valid test yielded a value of Young's modulus and subsequent strain amplitude and damping evaluation.

High temperature testing followed the guidelines of [7], while incorporating a two piece quartz spacer rod technique. Required rod lengths were determined in the normal manner, but were applied as the sum of a nominal length rod and a variable length rod. When a nominal length rod was joined to a specimen using ceramic glue, a change in the variable length rod

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TABLE I Composition, density and Young's modulus values

Specimen composition % Ti_5Si_3 and ID	Density ($kg\,m^{-3}$)		Young's modulus (GPa)
	Archimedes' method	Rule of mixtures	
10-1	5928	6059	377
10-2	5859	6059	375
20-2	5720	5808	326
30-1	5499	5558	316
30-2	5552	5558	321
40-1	5342	5307	307
40-2	5430	5307	312
50-1	5231	5057	304
50-2	5264	5057	304

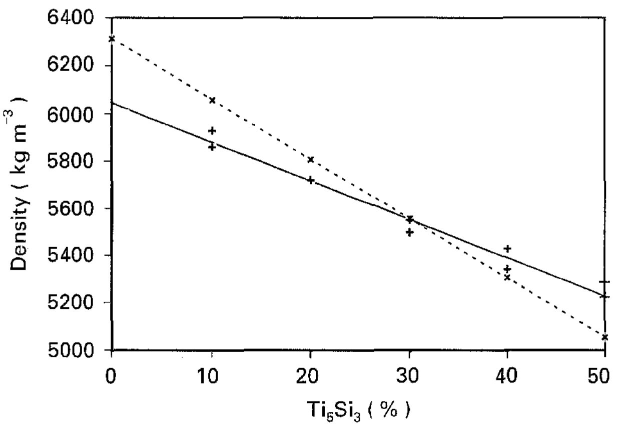

Figure 1 Density versus composition at room temperature: (+) Archimedes' method, (-- × --) rule of mixtures.

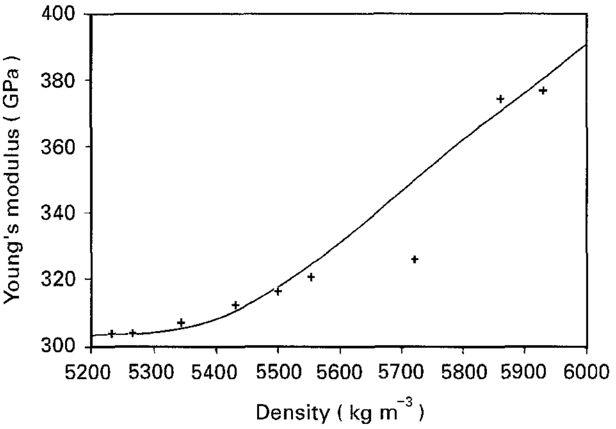

Figure 2 Young's modulus versus density at room temperature.

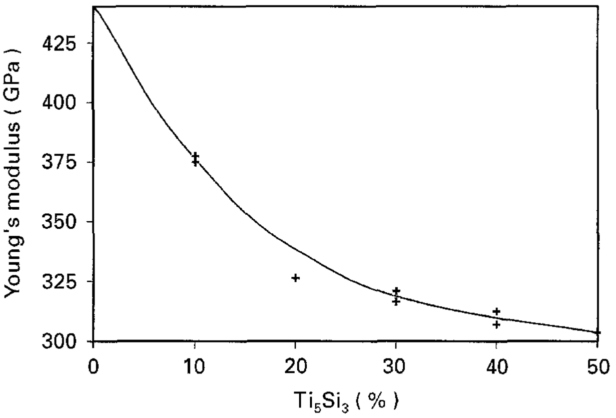

Figure 3 Young's modulus versus composition at room temperature.

determined the subsequent test temperature. Loctite glue joined the variable length rod to both the quartz crystals and the nominal length rod, so both joints could be dissolved easily with acetone. The nominal length was arbitrary, but was selected with care so that the variable length rods were not too small to handle nor so long that the new joint could not be kept below about 80 °C.

This technique allowed a specimen to remain attached to one rod as long as the ceramic glue joint remained intact. The longevity of this joint was increased significantly by allowing the specimen to cool slowly inside the furnace and by using a joint wrap when trimming the specimen (the joint wrap employed in this investigation consisted of a glass tube filled with candle wax). In addition, the rod mass and glue mass remained constant for each specimen with this technique.

One specimen of each composition was cemented to a nominal length rod, and subsequently tested at the first temperature using the shortest variable length rod. Invalid tests required adjustments in specimen length followed by a retest. Valid tests yielded values of Young's modulus, strain amplitude and damping. Testing at successive temperatures was accomplished by changing the variable length rod and repeating the procedure.

3. Results

Composition, density and Young's modulus values at room temperature for each specimen are shown in Table I. Density versus composition, Young's modulus versus density and Young's modulus versus composition are presented graphically in Figs 1–3, respectively. Linear regression determined the equations as listed in Table II. The equation for modulus versus density was calculated excluding the value for the 20% specimens. One of the 20% specimens broke while its length was being adjusted and was no longer suitable for PUCOT. The modulus of the second 20% specimen is lower than anticipated, possibly due to microcracks [8], and is therefore disregarded in the linear regression. Strain amplitude dependence of damping at room temperature is presented in Fig. 4.

High temperature testing results are presented in Figs 5–7 as temperature dependence of Young's modulus, strain amplitude dependence of damping and an Arrhenius plot of damping, respectively. Linear regression equations for Young's modulus with respect to temperature are listed in Table III.

4. Discussion

Unit cell dimensions [3, 9] for $MoSi_2$ and Ti_5Si_3 were used to calculated theoretical densities since

TABLE II Equations for the curve fits at room temperature

Density, ρ, versus composition, x	$\rho = -16.229x + 6041$ $r = -0.989$
Young's modulus, E, versus density, ρ	$E = -3.03 \times 10^{-6}\rho^3 + 5.18 \times 10^{-2}\rho^2 - 29.4231\rho + 55\,734.6$ $r = 0.996$
Young's modulus, E, versus composition, x	$E = -1.28 \times 10^{-2}x^3 + 0.168x^2 - 7.96x + 440.265$ $r = 0.998$

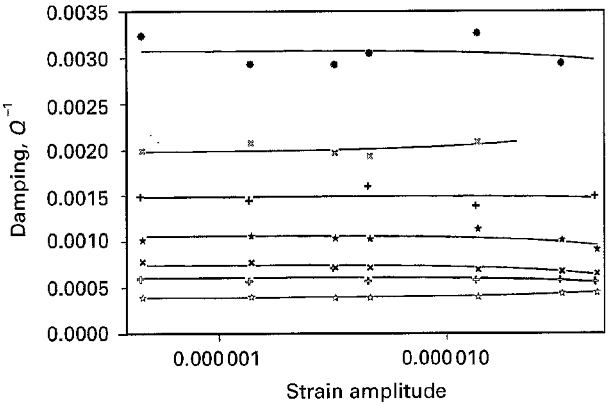

Figure 4 Damping versus strain amplitude at room temperature. Ti_5Si_3 (%): + (10-1), (✣) 10-2, (★) 30-1, (☆) 30-2, (×) 40-1, (✕) 40-2, (∗) 50-1.

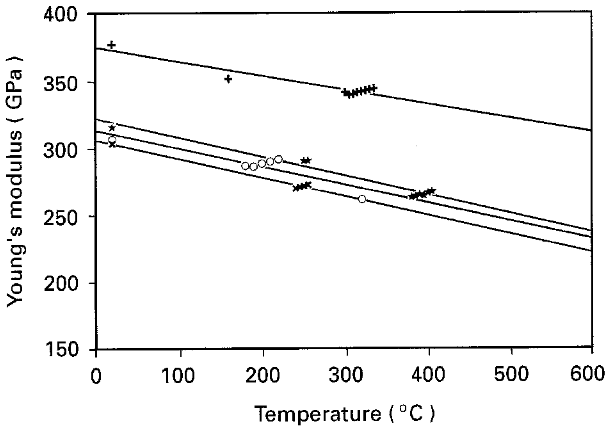

Figure 5 Temperature dependence of Young's modulus at Ti_5Si_3 (%): (+) 10, (★) 30, (○) 40, (×) 50.

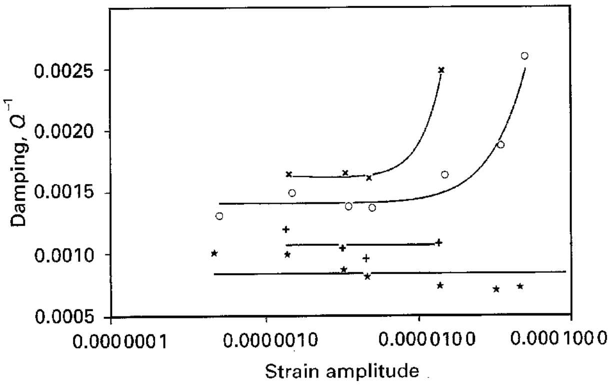

Figure 6 Damping versus strain amplitude at high temperatures for Ti_5Si_3 (%): (+) 10–1 at 160 °C, (★) 10-1 at 315 °C, (○) 30-1 at 380 °C, (×) 40-1 at 180 °C.

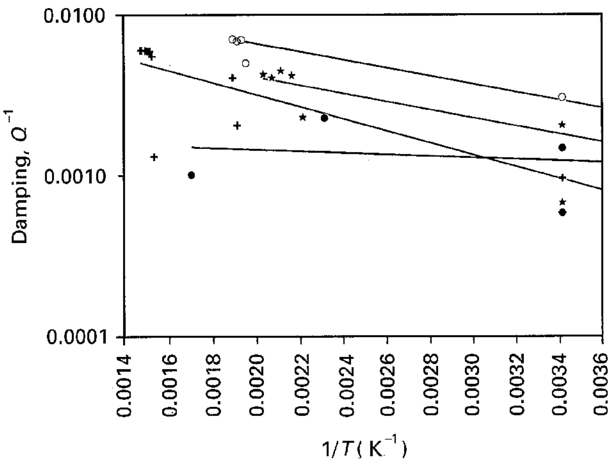

Figure 7 Damping versus reciprocal temperature for Ti_5Si_3 (%): (●) 10, (+) 30, (★) 40, (○) 50.

TABLE III Equations for the temperature dependence of Young's modulus, E, where r is the

Ti_5Si_3 (%)	E (GPa)	r
10	$-0.109T + 375.421$	-0.951
30	$-0.145T + 322.461$	-0.982
40	$-0.139T + 313.732$	-0.908
50	$-0.144T + 306.414$	-0.993

a published value for Ti_5Si_3 could not be located, and yielded 6309 and 3804 $kg\,m^{-3}$, respectively. Application of these values in rule of mixtures calculations produces results which compare favourably with the experimentally obtained densities (see Table I).

$MoSi_2$ has a modulus of 440 GPa [10]. Combining this value with the theoretical density and then looking at the plotted experimental data, we show that the composite's mechanical property values are dictated by the compound of largest volume per cent. This trend holds true for the five alloys tested, in all three comparison plots. The property values follow predictable paths based on composition.

The strain amplitude dependence of damping, corrected for the damping of the system, was evaluated. The damping of the specimens is small and independent of strain amplitude at room temperature, as expected for ceramics. This is because ceramics contain few dislocations and the dislocations are reluctant to move at room temperature. The limited data displayed in Fig. 6 suggest there may be some strain amplitude dependence at elevated temperatures.

Analysis of Fig. 5 reveals the temperature dependence of Young's modulus as linear and predictable for each composition, and shows the expected decrease in modulus with increasing temperature. The values of $[1/E(0)](\mathrm{d}E/\mathrm{d}T)$, where $E(0)$ is the value of Young's modulus at room temperature, range from -2.88×10^{-4} to $-4.74 \times 10^{-4}\,\mathrm{K}^{-1}$. These values can be compared with those given by Friedel [11] for many pure metals. His data lie in the range -4×10^{-4} to $-14 \times 10^{-4}\,\mathrm{K}^{-1}$. Clearly, the fall off in elastic modulus with increasing temperature for these ceramic specimens is at a smaller rate than that for the metals, reflecting the influence of the strong covalent and ionic interatomic bonding in ceramics. The Arrhenius plot of Fig. 7 is used in estimating the effective activation energy, H, of the material via the equation $Q^{-1} = Q^{-1}(0)\exp(-H/kT)$, where Q^{-1} is the damping, $Q^{-1}(0)$ is a reference value of damping and k is Boltzmann's constant. The activation energies fall in the range 0.03–0.06 eV atom^{-1}. This corresponds most likely to the increase in the thermal background contribution, kT, to the damping.

5. Conclusions

From this study of the measurements of density and dynamic Young's modulus in five $MoSi_2$–Ti_5Si_3 composites, the following conclusions are made.

1. The mass density of the composites decreases linearly with the Ti_5Si_3 content.

2. The mass density measured by the Archimedes' method is within 4.1% of that calculated by the rule of mixtures.

3. The dependences of Young's modulus on density and of Young's modulus on composition are approximately parabolic.

4. For most of the compositions and temperatures up to about 400 °C, damping is independent of strain amplitude.

5. Young's modulus decreases linearly with temperature, the values of $[1/E(0)](\mathrm{d}E/\mathrm{d}T)$ falling in the range -3 to $-5 \times 10^{-4}\,\mathrm{K}^{-1}$.

6. Arrhenius plots of damping lead to values of effective activation energy near kT.

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