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Author(s): John J. Petrovic, MST-8

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CERAMIC - SILICIDE COMPOSITES

John J. PETROVIC

Materials Science and Technology Division, Group MST-8, Mail Stop G770, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

The area of ceramic-silicide composites represents a merging of structural ceramics and structural silicides. Such ceramic-silicide composites can possess the desirable characteristics of both classes of compounds. Important structural ceramics are materials such as Si_3N_4, SiC, Al_2O_3, and ZrO_2, which possess covalent, ionic, or mixed covalent-ionic atomic bonding. An important structural silicide is $MoSi_2$, which possesses mixed covalent-metallic bonding. The arena of ceramic-silicide composites encompasses both composites where the structural silicide is the matrix and the structural ceramic is the reinforcement, and composites where the structural ceramic is the matrix and the structural silicide is the reinforcement. In the former area, $MoSi_2$-SiC, $MoSi_2$-ZrO_2, and $MoSi_2$-Al_2O_3 composites are discussed. In the latter area, Si_3N_4-$MoSi_2$ composites are described.

1. INTRODUCTION

Above 1000 °C, the choice of materials for structural applications in oxidizing and aggressive environments is limited to the classes of structural ceramics and structural silicides. Important structural ceramics include Si_3N_4, SiC, ZrO_2, and Al_2O_3. At the present time, the most important structural silicide is $MoSi_2$[1-5]. Since these structural ceramics are all thermodynamically stable with $MoSi_2$, there exists a significant potential for the synergistic development of ceramic-silicide composites with improved structural properties for elevated temperature applications. This paper describes interesting ceramic-silicide composites which have been explored to date.

2. SILICIDE MATRIX - CERAMIC REINFORCED COMPOSITES

The silicide $MoSi_2$ can best be described as a borderline ceramic-intermetallic compound[1]. It possesses a combination of properties which make it attractive as a high temperature structural material. It has a high melting point of 2030 °C, with excellent high temperature oxidation resistance. Unlike the structural ceramics, it exhibits a polycrystalline brittle-to-ductile transition in the vicinity of 1000 °C, and macroscopic compressive ductility below room temperature in some single crystal orientations[6]. Additionally, $MoSi_2$ can be electro-discharge machined, due to its electrical conductivity. However, for $MoSi_2$-based materials to be successful in elevated temperature structural applications, it is necessary to improve both high temperature strength and creep resistance, as well as low temperature fracture toughness[2]. This has provided the motivation for the development of $MoSi_2$ matrix-ceramic reinforced composites.

2.1. $MoSi_2$-SiC Composites

SiC has been used as a reinforcement for $MoSi_2$ matrix composites in both whisker[7-11] and particulate form[12-18]. SiC reinforcement has been observed to significantly improve the creep resistance and moderately improve the fracture toughness of $MoSi_2$.

Effects of SiC particulate reinforcement on the compressive creep behavior of $MoSi_2$-SiC composites are shown in Figure 1. Initially, the creep rate increases with increasing SiC reinforcement reaching a maximum at 20 vol.% SiC. However, at 30 vol.% SiC and especially at 40 vol.% SiC, the creep rate is markedly lower than that of pure $MoSi_2$. The reason for this maximum in creep rate with SiC content is the fact that the creep behavior of polycrystalline $MoSi_2$ is highly sensitive to grain size[2,19], and the $MoSi_2$ grain size of the $MoSi_2$-SiC composites decreases continuously with increasing SiC content[13].

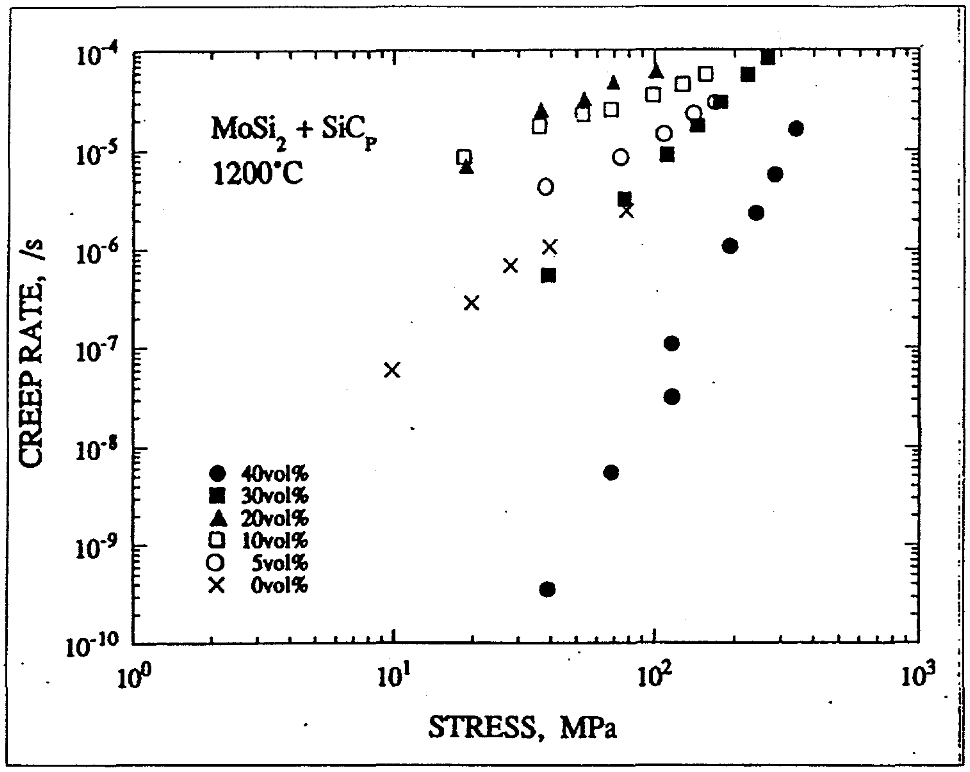


FIGURE 1

Creep rate of SiC particle-MoSi$_2$ matrix composites with different volume fractions of SiC phase[19].

For polycrystalline MoSi$_2$, creep rates increase rapidly with decreasing grain size. The grain size exponent observed for MoSi$_2$ is in the range of 5-8. For Nabarro-Herring creep, one expects a grain size exponent of 2, while for Coble creep a grain size exponent of 3 is expected. These grain size effects on the elevated temperature deformation of polycrystalline MoSi$_2$ are unusual and are not fully understood at the present time. However, they also occur in other intermetallic systems as well[19]. For MoSi$_2$, elevated temperature creep appears to be controlled primarily by dislocation glide/climb processes, as well as grain boundary sliding accommodated by dislocation plasticity.

As SiC reinforcement is added, the grain size effect of MoSi$_2$ dominates, and creep rates increase. However, above a certain amount of SiC addition, the composite reinforcement aspects of the SiC dominate, and creep rates then decrease. Thus, in MoSi$_2$-SiC composites, there is a competition between grain size effects and reinforcement effects.

It should be pointed out that, at constant SiC volume fraction reinforcement, creep rates of SiC whisker reinforced composites are approximately two orders of magnitude lower than those of SiC particulate reinforced composites[20]. This indicates that the SiC reinforcement shape morphology plays a significant role in creep resistance of the composites.

2.2. $MoSi_2$-ZrO_2 Composites

Transformation toughening is an important toughening mechanism associated with zirconia[21]. ZrO_2 transformation toughening effects have been employed to toughen $MoSi_2$ matrix-ZrO_2 particle composites[22,23]. Figure 2 shows the fracture toughness of these composites as a function of the amount of Y_2O_3 stabilizer in the ZrO_2 phase. Unstabilized ZrO_2 is observed to produce the maximum toughening effects in these types of composites. The unstabilized ZrO_2 tetragonal-to-monoclinic martensitic phase transformation occurs spontaneously upon cooling in the vicinity of 1100 °C. Thus, this transformation occurs above the brittle-to-ductile transition temperature of the $MoSi_2$ phase, where the $MoSi_2$ is still ductile. Since the ZrO_2 tetragonal-to-monoclinic phase transformation produces an approximately 4% expansional volumetric strain, this transformation effectively "pumps" dislocations into the $MoSi_2$ matrix, with potentially beneficial effects on the brittle-to-ductile transition temperature of $MoSi_2$-ZrO_2 composites, as well as on improvements to the fracture toughness.

2.3. $MoSi_2$-Al_2O_3 Composites

Al_2O_3 is an interesting ceramic reinforcement for $MoSi_2$, due to the fact that its thermal expansion coefficient is a very close match to the thermal expansion coefficient of $MoSi_2$. This means that laminate geometries of $MoSi_2$-Al_2O_3 composites may be fabricated without problems of residual stresses due to thermal

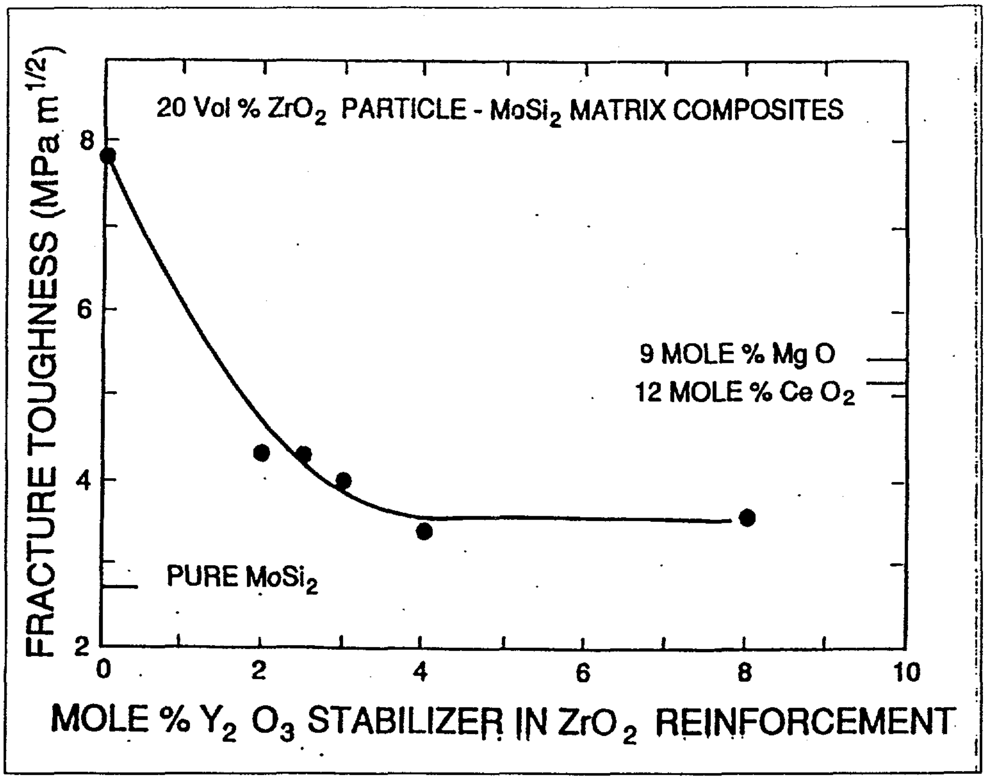


FIGURE 2
Fracture toughness of ZrO_2 particle-$MoSi_2$ matrix composites as a function of ZrO_2 stabilizer[22].

expansion coefficient mismatches. Such $MoSi_2$-Al_2O_3 laminate composites have been fabricated by plasma spray forming[24]. These laminate composites exhibit "graceful failure" at elevated temperatures, as shown in Figure 3. Here, a four-point bend test of the laminate composite was performed at 1400 °C. Rather than

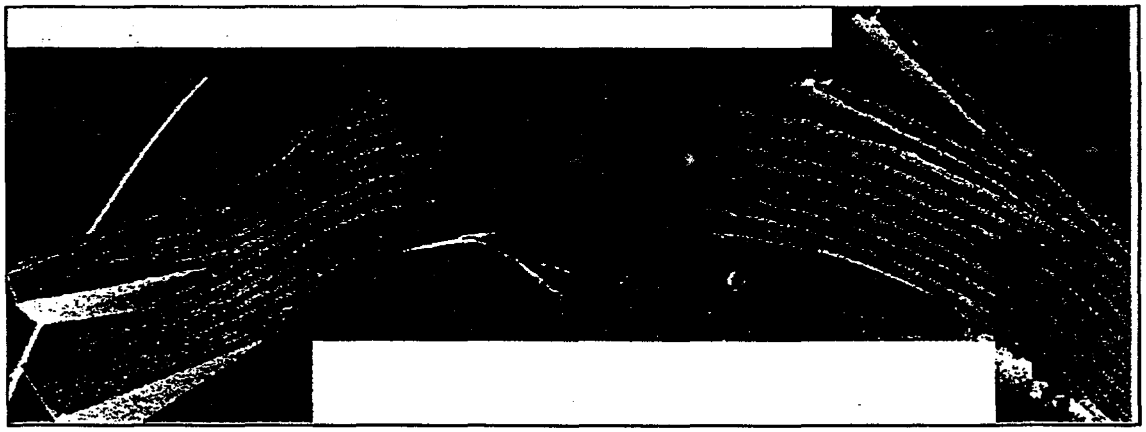


FIGURE 3
Bend test performed on a $MoSi_2$-Al_2O_3 laminate composite at 1400 °C. The light layers are $MoSi_2$ and the dark layers are Al_2O_3[24].

exhibiting catastrophic fracture, the $MoSi_2$-Al_2O_3 composite showed considerable plastic deformation and an "onion skin" type of failure. This was due to a combination of plasticity in the $MoSi_2$ layers and debonding at the $MoSi_2$-Al_2O_3 interfaces.

3. CERAMIC MATRIX - SILICIDE REINFORCED COMPOSITES

Silicides may be employed as reinforcements in ceramic matrix composites, to improve the properties of these materials. Two significant problems with structural ceramics are the following. First, ceramics are brittle materials. Structural ceramics such as Si_3N_4 and SiC are brittle over the full temperature range from room temperature to their elevated use temperatures. Second, it is difficult to machine these structural ceramics. Typically, expensive diamond machining is required, which increases the cost of ceramic components.

$MoSi_2$ possesses some characteristics pertinent to the above ceramic problems. It has a brittle-to-ductile polycrystalline transition in the neighborhood of 1000 °C. Thus, it is a ductile material at the elevated temperatures of use of structural ceramics. Essentially, at high temperatures, $MoSi_2$ represents a ductile, oxidation-resistant reinforcement phase for ceramic matrix composites. Additionally, $MoSi_2$ is an electrically conductive material, unlike the structural ceramics which are insulating. This means that if a ceramic matrix composite contains a suitably large volume fraction of the $MoSi_2$ phase, then the composite will become electrically conductive enough to be machinable by electro-discharge machining techniques, which are less costly than diamond machining.

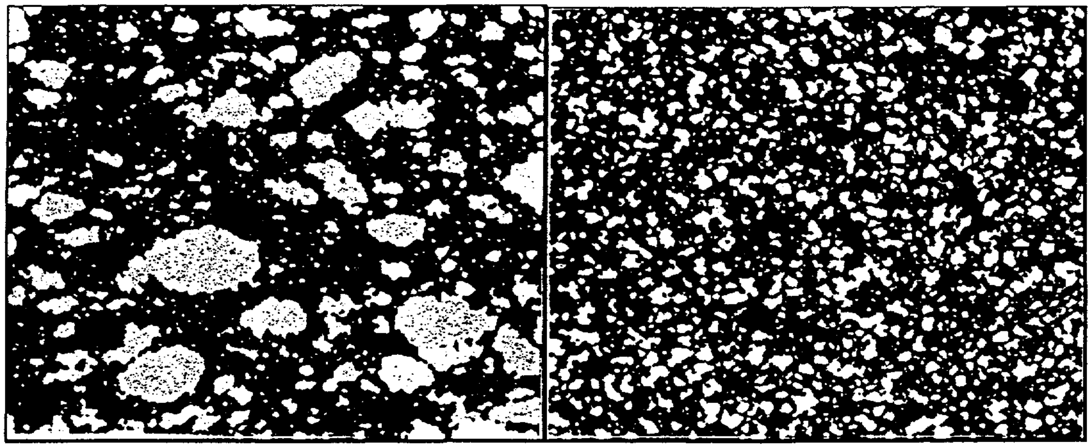
3.1. Si_3N_4-$MoSi_2$ Composites

The addition of a $MoSi_2$ phase to a Si_3N_4 matrix has the potential to produce composites with both improved fracture toughness and improved machinability, as well as improved oxidation resistance. $MoSi_2$ and Si_3N_4 are thermodynamically stable phases[25]. The Si_3N_4 phase is high temperature creep resistant, whereas the $MoSi_2$ phase may provide both low temperature toughening as well as high temperature ductile-phase toughening. The oxidation mechanisms of $MoSi_2$ and Si_3N_4 are similar because both form SiO_2 protective phases[26,27]. At suitable volume fractions of $MoSi_2$ phase, $MoSi_2$-Si_3N_4 composites can be electro-discharge machined because of the electrical conductivity of the $MoSi_2$ phase[28].

Because of the above advantages, the Si_3N_4-$MoSi_2$ composite system has seen an increasing interest[29-34]. Figure 4 shows the microstructures of Si_3N_4-$MoSi_2$ composites containing 30 vol.% $MoSi_2$ phase. It is interesting to note that despite the substantial thermal expansion coefficient mismatch between Si_3N_4 and $MoSi_2$, no microcracking is observed in the composite. This lack of microcracking is due to stress relief in the $MoSi_2$ phase as a result of plastic deformation upon cooling of the composite from the fabrication temperature[32].

The room temperature fracture toughness of Si_3N_4-$MoSi_2$ composites is shown in Figure 5. Room temperature toughening is sensitive to the size of the $MoSi_2$ phase. While the small $MoSi_2$ phase size produces relatively little fracture toughening, the larger $MoSi_2$ phase size produces substantial toughening, especially at the higher $MoSi_2$ volume fraction levels. This fracture toughening is thought to be due to internal stresses in the Si_3N_4-$MoSi_2$ composites which result from their thermal expansion coefficient mismatch[33].

The impression creep behavior of Si_3N_4-$MoSi_2$ composites is shown in Figure 6. With regard to creep behavior, the fine $MoSi_2$ phase composite exhibits better creep resistance than the coarse $MoSi_2$ phase composite. The fine phase composite is nearly as creep resistant as pure Si_3N_4 up to 30 vol.% amount of $MoSi_2$ phase. The reasons for this phase size effect on creep in Si_3N_4-$MoSi_2$ may be related to phase



10 μm $MoSi_2$ phase 3 μm $MoSi_2$ phase

FIGURE 4
Microstructure of Si_3N_4-$MoSi_2$ composites containing 30 vol.% $MoSi_2$ phase. The light phase is $MoSi_2$[32].

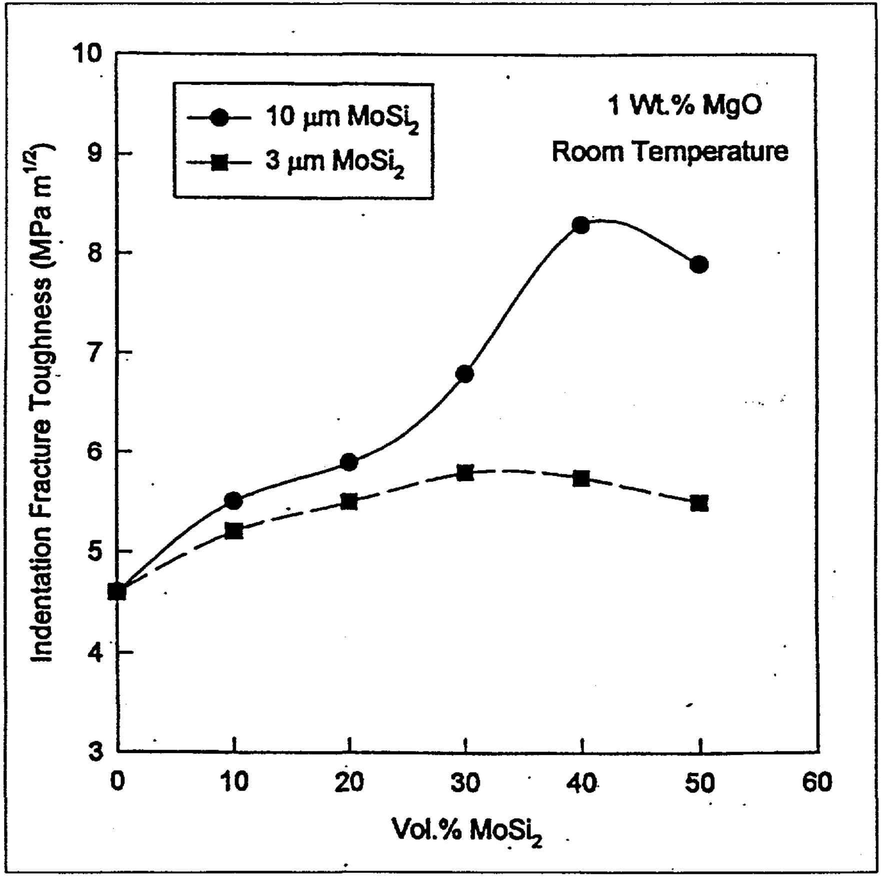


FIGURE 5
Room temperature fracture toughness of Si_3N_4-$MoSi_2$ composites, as a function of vol.% $MoSi_2$ phase[33].

boundary cohesion acting to minimize grain boundary sliding processes in both the Si_3N_4 and $MoSi_2$ phases, as the phase size is reduced. Increases in the phase boundary surface area/unit volume might also make dislocation climb/glide processes in the $MoSi_2$ phase more difficult because of the formation of dislocation pileups at the phase boundaries.

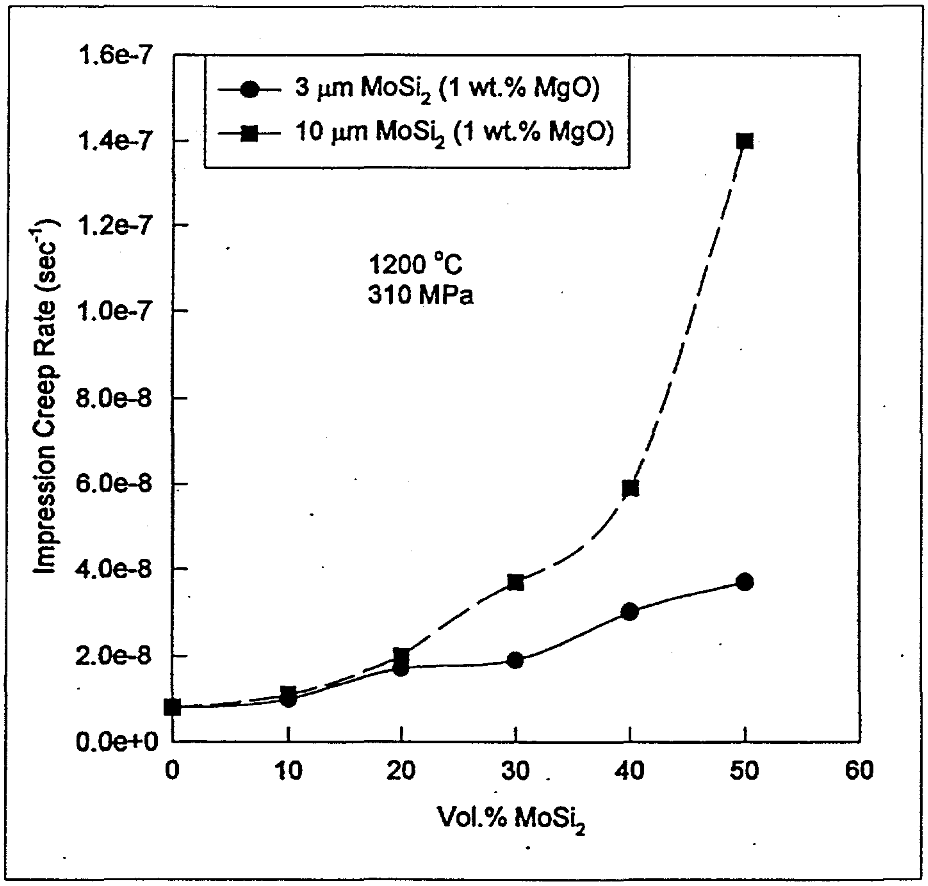


FIGURE 6

Impression creep behavior of Si_3N_4-$MoSi_2$ composites, as a function of vol.% $MoSi_2$ content[33].

ACKNOWLEDGEMENTS

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REFERENCES

1. J.J. PETROVIC, "High Temperature Structural Silicides", Ceram. Eng. Sci. Proc., **18** (1997), 3.

2. J.J. PETROVIC, "Mechanical Behavior of $MoSi_2$ and $MoSi_2$ Composites", Mater. Sci. Eng., **A192/193** (1995), 31.

3. J.J. PETROVIC AND A.K. VASUDEVAN, "Overview of High Temperature Structural Silicides", Mater. Res. Soc. Symp. Proc., **322** (1994), 3.

4. J.J. PETROVIC, "$MoSi_2$-Based High-Temperature Structural Silicides", MRS Bulletin, **XVIII** (1993), 35.

5. A.K. VASUDEVAN AND J.J. PETROVIC, "A Comparative Overview of Molybdenum Disilicide Composites", Mater. Sci. Eng., **A155** (1992), 1.

6. K. ITO, H. INUI, Y. SHIRAI, AND M. YAMAGUCHI, "Plastic Deformation of $MoSi_2$ Single Crystals", Phil. Mag. A, **72** (1995), 1075.

7. F.D. GAC AND J.J. PETROVIC, "Feasibility of a Composite of SiC Whiskers in an $MoSi_2$ Matrix", J. Amer. Ceram. Soc., **68** (1985), C200.

8. W.S. GIBBS, J.J. PETROVIC, AND R.E. HONNELL, "SiC Whisker-$MoSi_2$ Matrix Composites", Ceram. Eng. Sci. Proc., **8** (1987), 645.

9. D.H. CARTER, W.S. GIBBS, AND J.J. PETROVIC, "Mechanical Characterization of SiC Whisker-Reinforced $MoSi_2$", p. 977 in Proceedings of the Third International Symposium on Ceramic Materials and Components for Engines, The American Ceramic Society Inc., Westerville, Ohio, c. 1989.

10. J.J. PETROVIC AND R.E. HONNELL, "SiC Reinforced-$MoSi_2$/WSi_2 Alloy Matrix Composites", Ceram. Eng. Sci. Proc., **11** (1990), 734.

11. J.J. PETROVIC AND R.E. HONNELL, "SiC Reinforced-$MoSi_2$ Based Matrix Composites", Ceramic Transactions, **19** (1991), 817.

12. J.J. PETROVIC, R.E. HONNELL, AND A.K. VASUDEVAN, "SiC Reinforced-$MoSi_2$ Alloy Matrix Composites", Mat. Res. Soc. Symp. Proc., **194** (1990), 123.

13. A.K. BHATTACHARYA AND J.J. PETROVIC, "Hardness and Fracture Toughness of SiC-Particle-Reinforced $MoSi_2$ Composites", J. Am. Ceram. Soc., **74** (1991), 2700.

14. U. RAMAMURTY, A.S. KIM, S. SURESH, AND J.J. PETROVIC, "Micromechanisms of Creep-Fatigue Crack Growth in a Silicide-Matrix Composite with SiC Particles", J. Am. Ceram. Soc., **76** (1993), 1953.

15. U. RAMAMURTY, S. SURESH, AND J.J. PETROVIC, "Effect of Carbon Addition on Elevated Temperature Crack Growth Resistance in (Mo,W)Si_2-SiC_p Composite", J. Am. Ceram. Soc., **77** (1994), 2681.

16. J.D. FRENCH, S.M. WIEDERHORN, AND J.J. PETROVIC, "Tensile Creep and Creep Rupture of SiC-Reinforced $MoSi_2$", Ceram. Eng. Sci. Proc., **16** (1995), 129.

17. D.P. BUTT, D.A. KORZEKWA, S.A. MALOY, H. KUNG, AND J.J. PETROVIC, "Impression Creep Behavior of SiC Particle-$MoSi_2$ Composites", J. Mater. Res., **11** (1996), 1528.

18. Y. SUZUKI AND K. NIIHARA, "Effect of SiC Reinforcement on Microstructure and Mechanical Properties of $MoSi_2$", Sci. Eng. Comp. Mat., **6** (1997), 85.

19. C.R. FENG AND K. SADANANDA, "Grain Size Effect on the Creep Behavior of Monolithic $MoSi_2$", Mat. Res. Soc. Symp. Proc., **364** (1995), 1053.

20. K. SADANANDA AND C.R. FENG, "A Review of Creep of Silicides and Composites", Mat. Res. Soc. Symp. Proc., **322** (1994), 157.

21. D.J. GREEN, R.H.J. HANNINK, AND M.V. SWAIN, Transformation Toughening of Ceramics, CRC Press Inc., Boca Raton, Florida, c. 1989.

22. J.J. PETROVIC, A.K. BHATTACHARYA, R.E. HONNELL, T.E. MITCHELL, R.K. WADE, AND K.J. MCCLELLAN, "ZrO_2 and ZrO_2-SiC Particle Reinforced $MoSi_2$ Matrix Composites", Mater. Sci. Eng., **A155** (1992), 259.

23. Y. SUZUKI, T. SEKINO, AND K. NIIHARA, "Effects of ZrO_2 Addition on Microstructure and Mechanical Properties of $MoSi_2$", Scripta Metall. Mater., **33** (1995), 69.

24. A.H. BARTLETT, R.G. CASTRO, D.P. BUTT, H. KUNG, J.J. PETROVIC, AND Z. ZURECKI, "Plasma Sprayed $MoSi_2$/Al_2O_3", Industrial Heating, January 1996.

25. E. HEIKINHEIMO, A. KODENTSOV, J.A. VAN BEEK, J.T. KLOMP, AND F.J.J. VAN LOO, "Reactions in the Systems Mo-Si_3N_4 and Ni-Si_3N_4", Acta Metall. Mater., **40** (1992), S111.

26. T.A. KIRCHER AND E.L. COURTRIGHT, "Engineering Limitations of $MoSi_2$ Coatings", Mater. Sci. Eng., **A155** (1992), 67.

27. C.E. RAMBERG, P. BEATRICE, K. KUROKAWA, AND W.L. WORRELL, "High-Temperature Oxidation Behavior of Structural Silicides", Mater. Res. Soc. Symp. Proc., **322** (1994), 243.

28. O. THOMAS, J.P. SENATEUR, AND R. MADAR, "Molybdenum Disilicide: Crystal Growth, Thermal Expansion, and Resistivity", Solid State Commun., **55** (1985), 629.

29. J.J. PETROVIC AND R.E. HONNELL, "$MoSi_2$ Particle Reinforced-SiC and Si_3N_4 Matrix Composites", J. Mater. Sci. Lett., **9** (1990), 1083.

30. M.-Y. KAO, "Properties of Silicon Nitride-Molybdenum Disilicide Particulate Ceramic Composites", J. Am. Ceram. Soc., **76** (1993), 2879.

31. L.O. NORDBERG AND T. EKSTROM, "Hot-Pressed $MoSi_2$-Particulate-Reinforced Alpha-SiALON Composites", J. Am. Ceram. Soc., **78** (1995), 797.

32. J.J. PETROVIC, M.I. PENA, AND H.H. KUNG, "Fabrication and Microstructures of $MoSi_2$ Reinforced-Si_3N_4 Matrix Composites", J. Am. Ceram. Soc., **80** (1997), 1111.

33. J.J. PETROVIC, M.I. PENA, I.E. REIMANIS, M.S. SANDLIN, S.D. CONZONE, H.H. KUNG, AND D.P. BUTT, "Mechanical Behavior of $MoSi_2$ Reinforced-Si_3N_4 Matrix Composites", J. Am. Ceram. Soc., **80** (1997), 3070.

34. H. KLEMM, K. TANGERMANN, C. SCHUBERT, AND W. HERMEL, "Influence of Molybdenum Silicide Additions on High-Temperature Oxidation Resistance of Silicon Nitride Materials", J. Am. Ceram. Soc., **79** (1996), 2429.