

Synthesis and Properties of In-situ MoSi₂ / W composites

Dae-Kyu Jang and R. Abbaschian*

Korea Institute of Geology, Mining and Materials, Taejon 305-343 Korea

*Department of Materials Science and Engineering, University of Florida, Gainesville, FL32611, U.S.A.

MoSi₂/W 복합재료의 합성과 성질에 관한 연구

장 대규 · *R. Abbaschian

한국자원연구소, 자원활용·소재 연구부

*플로리다 대학교, 재료공학과, 미국

(1998년 7월 30일 받음, 1998년 8월 19일 최종수정본 받음)

초 록 MoSi₂에 W 분말을 첨가하여 MoSi₂/W 복합재료를 1600°C에서 3시간 동안 유지하면서 30MPa의 조건하에서 고온진공 가압기를 이용하여 제조하였으며, 텅스텐 분말의 첨가량이 (Mo)Si₂의 미세조직과 기계적 성질에 미치는 영향을 조사하였다. 텅스텐은 몰리브덴과 치환하면서 고용체 합금을 이루었으며, 입자의 크기는 텅스텐 분말의 첨가량이 증가할수록 감소하였다. 비커스 경도는 텅스텐 분말의 첨가량이 증가할수록 향상되었으나, 반면에 압흔과단 강도는 오히려 감소되었다. 10% 정도의 텅스텐 분말을 첨가하였을 때, 압흔과단 강도가 4.5MPa \sqrt{m} 로서 순수 MoSi₂의 2.7MPa \sqrt{m} 에 비하여 향상되었음을 알 수 있었다.

Abstract MoSi₂ / W composites were fabricated by vacuum hot press at 1600°C under 30MPa for 3 hrs. The effects of the amount of tungsten in the composites was explained in terms of the microstructure and mechanical properties. Although tungsten was mainly substituted to Mo atoms forming a complete solid solution of (Mo,W)_xSi_y (x=1, 5, y=2, 3), the grain size of composites became smaller with the increase of tungsten added. Vickers hardness was increased with the increase of tungsten content due to the solid-solution hardening. On the other hand, toughness of composites decreased sharply by increasing the amount of tungsten. Optimum tungsten amount was determined to be a 10 vol% of composite. Indentation fracture toughness was calculated to be 4.5 MPa \sqrt{m} in this composites, compared with 2.7 MPa \sqrt{m} in pure MoSi₂.

1. Introduction

Intermetallics are much interested in the use of next generation high-temperature structural materials due to the high melting temperature, low density and good corrosion resistance. Among intermetallics, MoSi₂ is one of best candidates for the application in high temperature materials. It has a high melting temperature of 2030°C, a density of 6.31g/cm³ and has an excellent high temperature oxygen resistance due to the formation of a surface coating of SiO₂ upon reaction with oxygen in the atmosphere.^{1~4)} An additional advantage of MoSi₂ materials is that it is ductile at the operational temperature,⁵⁾ as opposed to other competing structural materials. However, Monolithic MoSi₂ is not acceptable as a structural materials for engine applications because of its room temperature brittleness and low-temperature strength. Regarding the environmental stability, MoSi₂ exhibits an excellent resistance to oxidation, equivalent to that of SiC. This is proved by the successful utilization of MoSi₂ as heating elements capable of

operating in air, at the temperature of 1800°C. In particular, the best grade of MoSi₂ heating element, commercially known "Kanthal Super" is able to be operated up to 1900°C.⁶⁾

MoSi₂ has been synthesized by various methods such as conventional arc-melting, casting, mechanical alloying, sintering, SHS (Self-propagating High temperature Synthesis) and hot pressing.^{7~10)}

RHC (Reactive Hot Compaction) combines SHS with the application of pressure in order to increase densification.^{11~14)} The powders are blended, cold compacted, uniformly heated within a die to the reaction temperature under pressure. The exothermic reaction of the elemental powders initiates simultaneously at several sites through the compact. The reaction rate and product density depend on size and shape of reactant powders, compact green density, heating rate, applied pressure and processing atmosphere. RHC has been used previously by Doty et. al^{15,16)} to develop MoSi₂ composites. These composites exhibited higher fracture toughness than those synthesized using conventional

techniques.

SHS was used by soviet researchers almost thirty years ago.¹⁷⁾ The advantages of this process are numerous : high purity of products, low energy consumption, wide range of possible products and formation of near net shape structures.

In an attempt to improve mechanical properties of the MoSi₂, the reinforcement of MoSi₂ by compositing with SiC,^{18~21)} ZrO₂ particles,^{22~24)} and Nb fibers shows promising results.²⁵⁾

Efforts in the alloying of Molybdenum disilicide have included both substitutional and interstitial additions. Among the substitutional, tungsten and rhenium has been studied the most extensively. Substitutional alloying additions have been explored as a means of providing better mechanical properties as well as oxidation resistance on the basis of solid solution strengthening and altered crystal structure. Both Mo and W have b.c.c. structures with lattice constants *a*₀ of 0.3147 and 0.3165 nm and atomic radius of 0.201 and 0.202 nm respectively. Alloying MoSi₂ with W leads to complete solid solution strengthening is expected. WSi₂ has a high melting point (2160°C) and good oxidation resistance.

In this study, the monolithic MoSi₂ and MoSi₂ - W composites were fabricated using reactive hot compaction in a vacuum atmosphere. The microstructure and properties of these materials were comparatively characterized and solid solution hardening effects of tungsten powder in the composites were evaluated.

2. Experimental Procedure

The samples used in this study were fabricated by reactive hot compaction (RHC). The starting materials for hot pressing are MoSi₂ (99.9% pure, -325mesh, Johnson Matthey) and W powder (99.9% pure, 2-3μm, Ceramic Co.). For comparison, the powders were mixed in the specified proportions for 3 hours using a ball mill. The powder was initially loaded in the dies applying low pressure to maintain a sufficient open porosity. The samples were then vacuum hot pressed at 300MPa in a boron nitride coated graphite die. The powder compact-

ed were the heated 1600°C at the rate 30°C/min. and held at this temperature for three hour.

Specimens for microstructural characterization and vickers indentation measurements were cutting by EDM (Electro Discharge Machine), ground and polished by 1μm diamond suspension. The phase analysis of the samples was carried out using a Philips ADP3720 diffractometer operated at 40kv and 30mA with Cu K_α radiation. The samples were examined by optical metallography, SEM (Scanning Electron Microscopy, Jeol 6400) with an EDS (Energy Dispersive x-ray analysis System)

Vickers microhardness indentations were made on the surfaces of the samples polished to 1μm diamond finish. The indentation loads spanned 7kg (68.6N) for contact time of 15s, with a minimum of 4 indentations per indent load per sample. The minimum indentation loads were selected so as to achieve a minimum value 2 for the ratio of half penny crack radius (*c*) and half the diagonal of the vickers impression, a requirement recommended in practice for toughness measurement by indentation. The impression size and radial crack length were carefully measured. The fracture toughness (*K_{IC}*) were calculated by using Anstis' equations.²⁶⁾ The Young's modules of the composites were calculated using literature values for MoSi₂ [440GPa] and WSi₂ [471GPa] and assuming the rule of mixture behavior. Table 1. Summarizes the processing parameters and the nominal compositions of the alloys studied.

3. Results and Discussion

Phase analysis

In the MoSi₂ / WSi₂ system, x-ray diffraction analysis also showed that single phase MoSi₂ - WSi₂ solid solution was synthesis as a result of reactive hot compaction.²⁷⁾ Fig. 1. shows the XRD patterns of MoSi₂ / W composites for different additions of tungsten content. MoSi₂ / W composites did not show the presence of any unreacted tungsten in Fig. 1. Nevertheless, in the case of the MoSi₂ / W system, the characteristic eutectic alloy between the (Mo · W)₂Si₂ and (Mo · W)₃Si₃ was observed. X-ray phase examination of the specimen

Table 1. Alloy designation and compositions of the alloys studied.

Alloy Designation	Material	Hot pressed Temperature(°C)	Holding Time
MW0	Monolithic MoSi ₂	1600°C	3hr.
MW1	MoSi ₂ + 5vol.% W	1600°C	3hr.
MW2	MoSi ₂ + 10vol.% W	1600°C	3hr.
MW3	MoSi ₂ + 30vol.% W	1600°C	3hr.
MW5	MoSi ₂ + 50vol.% W	1600°C	3hr.

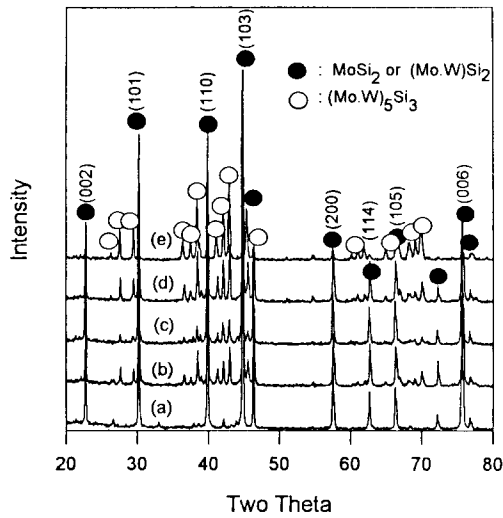


Fig. 1. X- ray diffraction patterns of MoSi₂ / W composites for different additions of tungsten contents. (a) Monolithic MoSi₂, (b) MoSi₂ + 5vol.% W (c) MoSi₂ + 10vol.% W (d) MoSi₂ + 30vol.% W (e) MoSi₂ + 50vol.% W

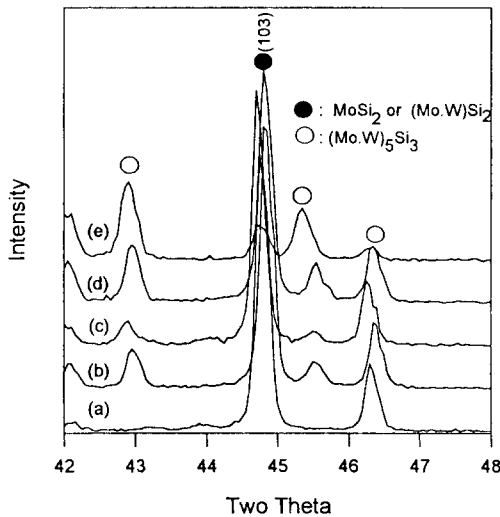


Fig. 2. X-ray diffraction patterns for the MW0, MW1, MW2, MW3 and MW5 samples from 42 to 48 two theta.

suggests that the amount of (Mo · W)₅Si₃ formed increased considerably with increasing of the tungsten content. It is clearly shown that the amount of (Mo · W)₅Si₃ formed increases considerably with increasing of the tungsten content.

An X-ray diffraction peak of (Mo.W)_wSi_y composites is demonstrated on the extended scale in Fig. 2. It can be seen that peaks broadens with increasing tungsten content. X-ray analysis confirmed the formation of both (Mo · W)Si₂ and (Mo · W)₅Si₃ solid solutions by adding tungsten. It can be seen that major peak (103), obtained from the tetragonal crystal structure of MoSi₂, shifted to the low angle side resulting from the tungsten dissolution.

Since both MoSi₂ and WSi₂ have the tetragonal struc-

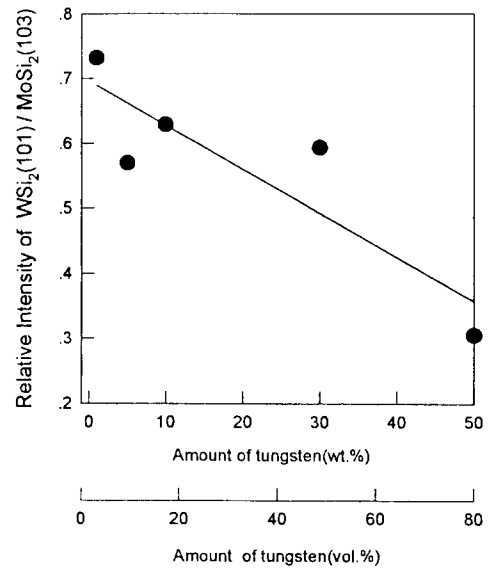


Fig. 3. Comparison of relative intensity for WSi₂(101) and MoSi₂(103) alloys.

ture with similar lattice constants, the X-ray diffraction peaks appear at close angles. From the x-ray diffraction patterns, we determined the relative intensity of WSi₂ major peak (101)/MoSi₂ major peak (103) for the alloy. Fig. 3. compared of experimental relative intensity for WSi₂ and MoSi₂ alloys. It can be seen from Fig. 3. with increasing tungsten content, the relative intensity sharply decreased. This is due to the stress during solid-solutions or forming of second phase (Mo · W)₅Si₃.

Microstructure

The monolithic MoSi₂, and MoSi₂ / W alloys were prepared by reactive hot compaction (RHC) in the vacuum atmosphere. The typical microstructure of the RHCed samples are given in Fig. 4. Optical metallography was relatively uniform in Fig. 4.(a). Fig. 4.(d) clearly shows a microstructure containing two phase. one is a MoSi₂ phase. The other one is a (Mo · W)_xSi_y (x=1, 5 y=2, 3) phase. Polarized microscopy indicated that dark phase increase with increasing tungsten content. The grain size of the MW5 alloy is about 3~4μm with the mean grain size close to tungsten powder. It is noteworthy that the grain size of (Mo · W)_xSi_y (x=1.5, y=2.3) is smaller than that in monolithic MoSi₂. It is indicated that alloying MoSi₂ with W cause an overall decrease in the self-diffusion rates. It was confirmed that small white particles in the Fig. 4. (d) are silica particle (originally present as a surface layer on the powders) by EPMA. Presence of silica in MoSi₂ alloys can be a problem in mechanical properties.

Fig. 5. shows a scanning electron micrograph of hot

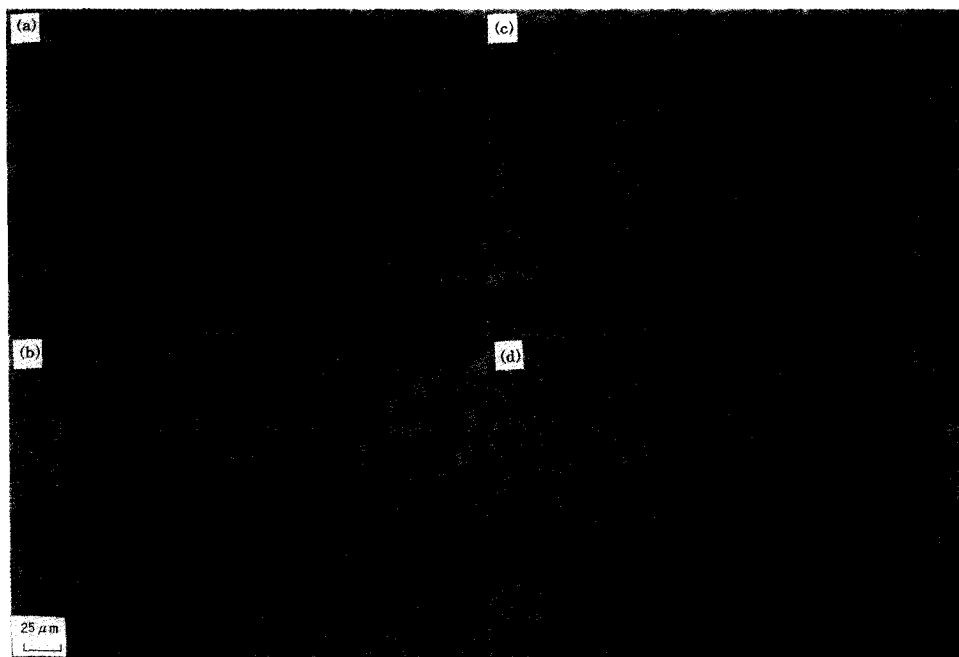


Fig. 4. Optical micrographs of specimen using reactive hot compaction in the vacuum atmosphere. (a) Monolithic MoSi₂ (b) MoSi₂ + 10vol.% W (c) MoSi₂ + 30vol.% W (d) MoSi₂ + 50vol.% W

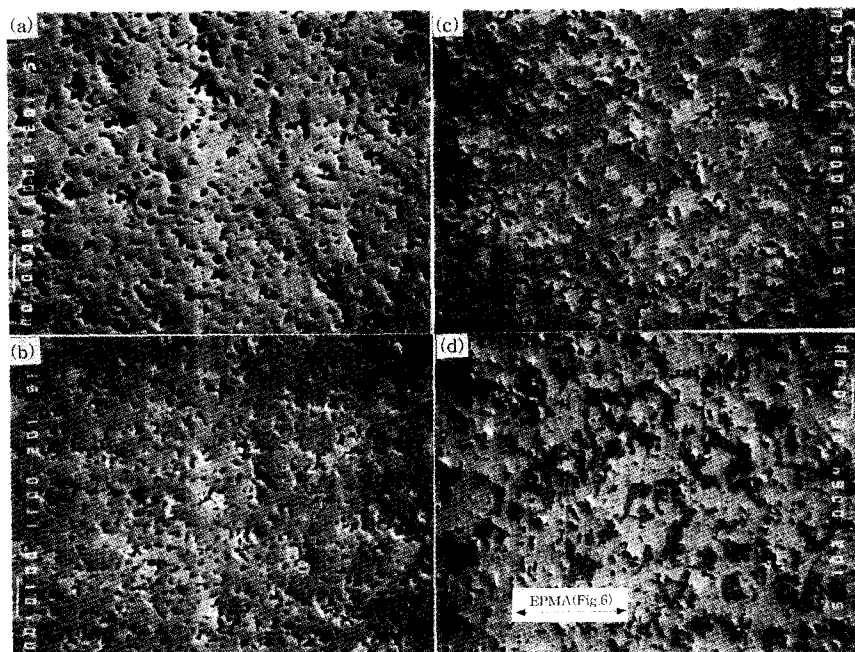


Fig. 5. Scanning electron micrograph of specimen using reactive hot compaction in the vacuum atmosphere : (a) Monolithic MoSi₂ (b) MoSi₂+ 10vol.% W (c) MoSi₂ + 30vol.% W (d) MoSi₂ + 50vol.% W

pressed specimen MW0, MW2, MW3 and MW5. As Fig. 5. indicated that the $(Mo \cdot W)_xSi_y$ ($x=1, 5, y=2, 3$) solid solution with W powder were inhomogeneous with large variation in its composition. The variation in the colour of grains signifies a variation in the composition of the disilicide solid solution. As seen in the Fig. 5. (b, c, d), MoSi₂ and W reacted extensively during the processing. Microstructure of the MoSi₂ / W composites showed less extensive grain growth in the alloy than in

monolithic MoSi₂. This might suggest that substitutional solid solution alloying with W influence either the grain energies or grain boundary mobilities.

Fig. 6. shows a compositional profile by EPMA between bright phase and dark phase from MW5 alloy. The reaction product was determined to be $(Mo \cdot W)_xSi_y$ ($x=1, 5, y=2, 3$). The formation of $(Mo \cdot W)_xSi_y$ during the reaction of MoSi₂/W has been attributed to the consumption of Si to form $(Mo \cdot W)_xSi_y$ renders the

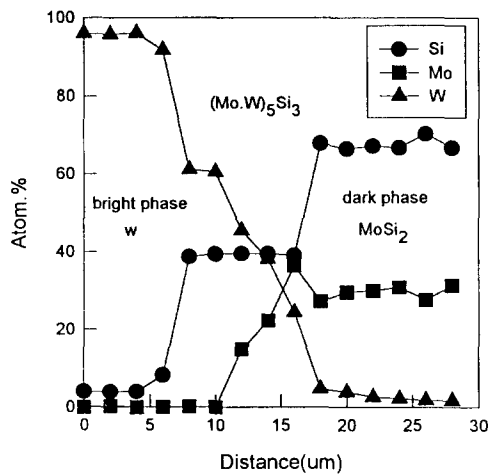


Fig. 6. Corresponding compositional profile by EPMA between darken phase and bright phase.

materials Mo/W rich leading to the formation of $(\text{Mo} \cdot \text{W})_5\text{Si}_3$. EPMA results from this sample clearly shows that the dark area contains more silicon and the bright phase, more tungsten. A comparison of the two micrographs reveals that the second phase tend to located at the grain boundaries and triple points.

Mechanical properties

It is well known that the introduction of solute atoms into solvent lattice produces a solid-solution hardening due to the lattice misfit. Early studies²⁸⁾ of the increase in hardening resulting from solid-solution additions showed that the hardness increase varies directly with the difference in the size of the solute and solvent atoms, or with the change in lattice parameter resulting from the solute addition. The solute additions are to raise the yield stress. Moreover, the improvement in mechanical properties was found to be dependent on a particle size, particle distribution, and volume fraction of the reinforcements.

Fig. 7. shows the variation of the vickers hardness as a function of reinforcement content of the composites. For comparison, the hardness of the composites as predicted by a simple rule of mixtures is also plotted. It should be noted that while the hardness values of Monolithic MoSi_2 ($4 \sim 5 \mu\text{m}$) studied in this investigation is 960Hv. Indeed, previous studied²³⁾ on monolithic MoSi_2 have shown the hardness to be structure sensitive, with slight increase with decreasing grain size. The results also show that hardness of the $(\text{Mo} \cdot \text{W})_5\text{Si}_3$ ($x=1, 5, y=2, 3$) composites increase with increasing W content. The hardness of the in-situ composites was a slightly higher than the other researcher.¹⁾

Fig. 8. shows the variation of the fracture toughness as a function of reinforcement content for the in-situ

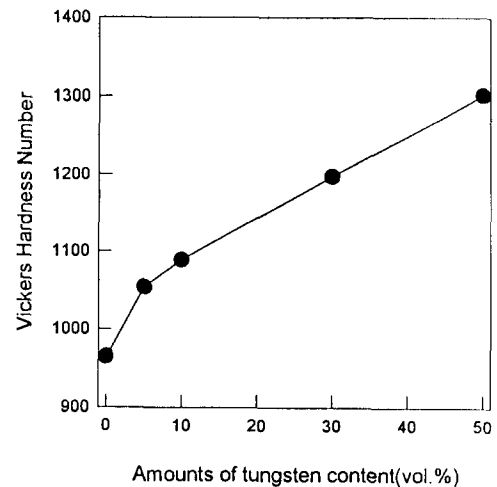


Fig. 7. Variation of the microvickers hardness as a function of reinforcement content of the composites at room temperature.

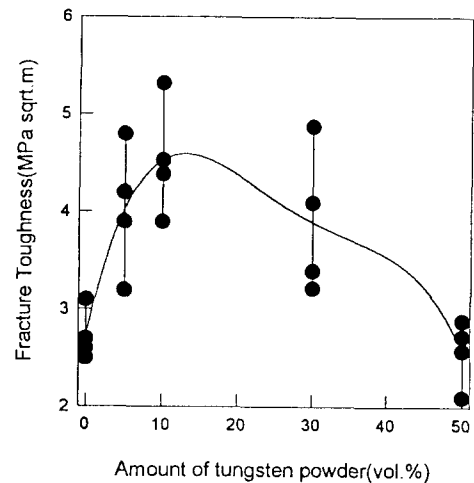


Fig. 8. Variation of the fracture toughness as a function of reinforcement content for the in-situ processed.

processed. Unlike the hardness, the indentation fracture toughness is not proportionally related with the content. Toughness increases with a increasing the tungsten content up to 10 vol.%, whereas further increasing tungsten decreases fracture toughness. In fact, the grain size of MoSi_2 showed little effect on the toughness of composites. This reason for this may be: the fracture toughness is controlled by a number of factors, and cannot be improved by only reducing the grain size. It found that toughness was optimized at 10vol.% content tungsten powder. At this level, indentation fracture toughness was increased from $2.7\text{MPa} \sqrt{m}$ in the monolithic MoSi_2 to approximately $4.5\text{MPa} \sqrt{m}$ in the MoSi_2 composites. This value is similar to previous studies²⁹⁾ on W particle - reinforced MoSi_2 composites. In the case of MW5 ($\text{MoSi}_2 + 50\text{vol. \% W}$), there are lots of second phase formation of $(\text{Mo} \cdot \text{W})_5\text{Si}_3$ phase. The formation of an Me_5Si_3 ($\text{Me} = \text{Mo} \cdot \text{W}$) interface reaction

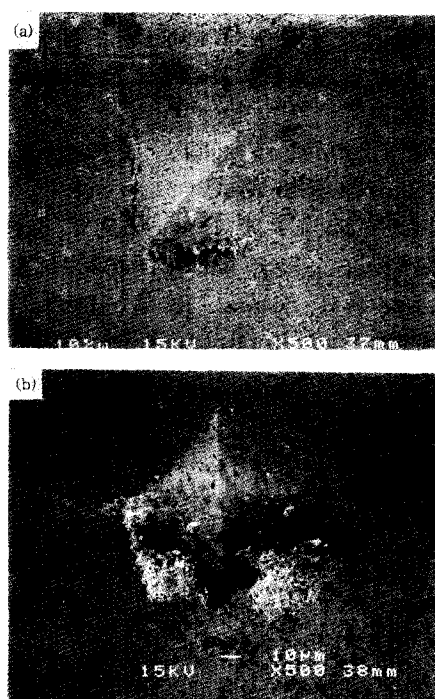


Fig. 9. Crack propagation modes by vicker's indentation with a load 7kg. (a) MoSi₂ + 10vol.% W (b) MoSi₂ + 50vol.% W.

layer by silicon diffusion into the metal is detrimental to the composites's mechanical properties. This may provide a means to improve the high-temperature creep resistance.

Fig. 9. show the micrographs of indentation cracks in materials in MW2 and MW5. In the case of MW2 (MoSi₂ + 10vol.% W), microcracking showed a little around the vickers indenter. On the other hand, MW5 alloy showed lots of extensive micro cracking around the vickers indenter. The morphology of these cracks reflect that this propagations were controlled by different mechanism. As seen in the Fig. 5., the presence of the (Mo · W)₅Si₃ and pores weakens the grain boundary. The silica particles present inside grains and at grain boundaries apparently did not interfere with crack propagation. In this studies, more silica particles were found by EPMA in the composites. Under the given conditions, the toughening effect obtained from MW2 samples was found much significant than that obtained from MW5.

4. Conclusion

The following conclusions can be drawn from the present investigation. The solid - solution hardening of MoSi₂ alloy is necessary to understand the reaction that occur in various composition based on MoSi₂. The synthesis of in-situ MoSi₂ / W alloy did not show the presence of any unreacted tungsten. Microstructure

and X-ray analysis showed that the MoSi₂ / W alloys formed solid solutions. The vickers hardness increased largely by the addition of most soluble elements. Nevertheless, the toughening effects of composites decreased largely by the increasing of tungsten. Indentation fracture toughness of alloy was almost twice greater than pure MoSi₂. It was shown that toughness was optimized at a 10vol% content of tungsten powder. At this tungsten level, indentation fracture toughness was increased from 2.7MPa \sqrt{m} in the monolithic MoSi₂ to approximately 4.5MPa \sqrt{m} in the composites. Porosity in one of the two component materials at the interface could lead to a low fracture toughness of the interfacial region due to the crack propagation along the weak path.

Acknowledgements

The authors is grateful to the support of professor Reza. Abbaschian at Department of Materials Science and Engineering, University of Florida, Gainesville, FL32611, U.S.A.

References

1. J. L Chermant and F.osterstock, J. Mater. Sci., Vol. 11 (1971) 1939-51
2. P. Hing and G. W. Groves, J. Mater. Sci., Vol. 7 (1972) 427-34
3. William J. Boettinger, Mater. Sci. and Eng., A155 (1992) 33-44
4. Gokhale, A and G. J. Abbaschian, Journal of phase Equilibira, 1991.12: p.493-498
5. K.. Kmura, M. Nakamura and T. Hirano, J. Mater. Sci., 25 (1990) 2487
6. Kanthal, Kanthal Super Catalog. 1996. Hallstahammar, Sweden:Kanthal Furnace products
7. R.B. Schwarz, S. R. Srinivasan, J. J. Petrovic and C. J. Maggiore, Materials Science and Engineering, A1559 (1992) 75-83
8. D. E. Alman and R. D. Govier, Scripta Materialia, Vol. 34, No. 8, (1996) 1287-1293
9. I. J. Shon, Z. A. unir , K.Yamazaki and K. Shoda, J. Am. Ceram. Soc., 79 (7), (1996) 1875-80
10. Seetharama C. Deevi, Mater. Sci. and Eng. A149 (1992) 241-251
11. L. Xiao, Y. S Kim and R. Abbaschian, Mater. Sci. and Engi. A144 (1991) 277-285
12. D. A. Hardwick, P. I. Martin and R. J. Jerina, Acta Metall. et Mater., 42 (1994) 3741
13. D. E. Alman and N. S. Stoloff, Scripta Metall. et

- mater., **28**(1993) 1525
14. D. E. Alman and C., P. Dogan, *Scripta Metall. et mater.*, **31** (1994) 273
 15. A. Gomez, H.F. Wang, H. Doty, and R. Abbaschian in *Proc. of the Second Pacific Rim International Conference on Advanced Materials and Processing*
 16. A. Gomez, Master's Theses, University of Florida, Dept. of Materials Science and Engineering, Gainesville, Florida 32611, 1994
 17. Merzhanov, A. G., Borovinskaya, I.P. *Synthesis of refractory Inorganic Compounds; Certif.255221*, (1967) 1170735
 18. J. M. Yang, S. M. Jeng, *Mat. Res. Soc. Symp. Proc.* 194, San Francisco, CA, (1990) 139-146
 19. Arun K. Bhattacharya and John J. Petrovic. *J. Am. Ceram. Soc.* **74**, (1990) 2700-2703
 20. Frank D. Gac and John J. Petrovic, *J. Am. Cer. Soc.* **68**, (1985) C-200-C-201
 21. W. S. Gibbs, John J. Petrovic and R. E. Honnell, *Ceram. Eng. Sci. Proc.* **8** (1987) 645-648.
 22. J. J. Petrovic, A. K. Bhattacharya, R.E. Honnell, T. E. Mitchell, R.K.Wade, *Mat. Sci. Eng.* **A155** (1992) 259-266
 23. Arun K. Bhattacharya and John J. Petrovic, *J. Am. Cer. Soc.* **75**, (1992) 23-27
 24. 18. J. J. Petrovic, R. E. Honnel and T. E. Mitchell, *Ceram. Eng. Sci. Proc.* **12**(1991) 1633-1642
 26. T.C. Lu, A.G. Evans, R. J. Hecht, and R. Mehrabian, *Acta Metal. Mater.* **39**, (1991) 1853-1862
 27. J. Besson, M. Degraef, J.P.A Lofvander, and S. M. Spearing, *J. Mat. Sci.* **27**, (1992) 4160-4168
 28. A. L. Norbury, *Trans. Faraday Soc.*, vol. **19**, (1924) 506-600
 29. L.C. Chen, D. Brooks, R. J.Lederich and W. O. Soboyejo, *Proc. Symp. on Intermetallic Composites III*, vol. **350**, (1994) 350