

Improvement of Impact Properties for Nb/MoSi₂ Laminate Composites by the Interfacial Modification (II)

Sang-Pill Lee

Institute of Advanced Energy, Kyoto University and CREST-ACE, Japan

Han-Ki Yoon*

Department of Mechanical Engineering, Dong-Eui University

The thermodynamical estimation of the interfacial reaction and the impact properties of Nb/MoSi₂ laminate composites containing SiC, NbSi₂ or ZrO₂ particles are investigated. Laminate composites, which comprise alternating layers of MoSi₂ with the particle and Nb foil, were fabricated by the hot press process. It is clearly found out that the interfacial reaction of Nb/MoSi₂ can be controlled by the addition of ZrO₂ particle to the MoSi₂ phase. The addition of ZrO₂ particle increases both the impact value and the sintered density of Nb/MoSi₂. The suppression of the interfacial reaction is caused by the formation of ZrSiO₄ in MoSi₂-ZrO₂ matrix mixture.

Key Words : Nb/MoSi₂ Laminate Composites, Impact Properties, Interfacial Modification.

1. Introduction

Several intermetallic compounds have been developed for a new approach of turbojet and hypersonic engines in aerospace vehicles as well as various structural applications. (Shah et al., 1992 ; Ward and Culbertson, 1994) In particular, molybdenum disilicide (MoSi₂) has been recognized as an attractive structural material for high temperature services, because of its low density, excellent oxidation resistance and thermo-dynamical compatibility. (Vasudevan and Petrovic, 1992 ; Petrovic et al., 1990 ; Meschter and Schwartz, 1989) However, for practical applications of MoSi₂, some problems have to be solved such as its brittle characteristics at the temperature below 1000°C and the strength reduction at a high temperature over 1200°C. Several studies have indicated that lamination toughening with ductile

ligaments, which is based on the crack bridging mechanism, can play an important role in improving the fracture properties of brittle materials. (Rawers and Perry, 1996 ; Kajuch et al., 1995 ; Yoon et al., 1995 ; Choi and Kinloch, 1998) The previous study showed that lamination of MoSi₂ with Nb foil sufficiently improved the fracture energy of MoSi₂ material. (Lee et al., 1998) However, the interfacial reaction layer must be suppressed for the optimum design of Nb/MoSi₂ laminate composites, since this layer tends to decrease the fracture energy by constraining the plastic deformation of Nb foil. Recently, the efficiency of oxide coatings applied to Nb foil has been investigated. But this approach compromises the toughness of the materials, due to the weakness of the interfacial bonding. (Xiao and Abbaschian, 1992 ; Lu et al., 1991)

The purpose of the present work is to investigate the effect of the addition of SiC, NbSi₂ and ZrO₂ particles on the thickness of the interfacial reaction layer and the impact properties of Nb/MoSi₂ laminate composites. In addition, the suppression mechanism of the interfacial reaction between MoSi₂ and Nb is evaluated.

* Corresponding Author,

E-mail : hkyoon@hyomin.dongueui.ac.kr

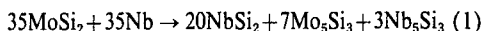
TEL : +82-51-890-1642 ; FAX : +82-51-890-1619

Department of Mechanical Engineering, Dong-eui University, 24, Kaya-dong, Pusanjin-gu, Pusan, 614-714, Korea. (Manuscript Received January 24, 2000;

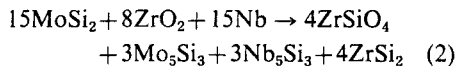
Revised May 22, 2000)

2. Thermodynamical Prediction of Interfacial Reaction

In the previous work, two distinct reaction layers, (Nb, Mo)Si₂ and Nb₅Si₃, were identified in the interfacial region of Nb/MoSi₂ laminate composites fabricated at 1350°C. (Lee et al., 1998) Based on these results, the chemical reaction between Nb and MoSi₂ was shown as follows:



In this equation, the (Nb, Mo)Si₂ phase is assumed to approximate NbSi₂, because the former contains a small amount of Mo element (about 2 at %). The strong chemical behavior of Si to form silicides results in the growth of the interfacial reaction layer. Therefore, the interfacial reaction between Nb and MoSi₂ may be controlled by the suppression of Si diffusion from the MoSi₂ phase to the Nb phase. The addition of ZrO₂ particles into MoSi₂ is thermodynamically expected to reduce the interfacial reaction of Nb/MoSi₂. If Si element is isolated from MoSi₂, ZrO₂ particles in MoSi₂ tend to form the ZrSiO₄ phase before reacting with Nb. Consequently, the diffusion of Si element can be decreased relative to that in Nb/MoSi₂. From this concept, the interfacial reaction (1) of Nb/MoSi₂ is transformed into the reaction (2) by the addition of ZrO₂. The ZrSi₂ phase will be formed as a product of the reaction (2). Furthermore, the NbSi₂ phase in the reaction (1) vanishes at the interface of Nb/MoSi₂-ZrO₂.



Standard free energy changes for reactions (1) and (2) calculated at 1350°C are -1.73×10^6 (J/mol) and -4.59×10^5 (J/mol), respectively. The resulting free energies will have negative values, and interfacial reactions will therefore be possible. These thermodynamical results demonstrate that the addition of ZrO₂ particles into MoSi₂ can decrease the thickness of the reaction layer in Nb/MoSi₂.

3. Experimental Procedures

The four matrices used in this experiment were MoSi₂, MoSi₂-NbSi₂, MoSi₂-SiC and MoSi₂-ZrO₂. The sizes of MoSi₂, NbSi₂, SiC and ZrO₂ particles were 2.8 μm, 3.5 μm, 3.0 μm and 0.1 μm, respectively. The mixed powder for each matrix was prepared by ball milling. The milling speed and the holding time were 150rpm and 3.6ks, respectively. The volume fraction of NbSi₂ and SiC particles dispersed in MoSi₂ powder was held to 20vol %. The volume fraction of ZrO₂ (containing 5.14wt% Y₂O₃) particle was varied from 10vol % to 30vol %. All laminate composites were fabricated successfully by vacuum hot pressing for 3.6 ks at 1350°C under 30 MPa. The thickness and the volume fraction of high purity Nb foil (99.99mass%) involved in these laminate systems were 0.2mm and 10vol%, respectively.

Impact properties of sintered matrix materials and their laminate composites were evaluated at room temperature using an instrumented Charpy

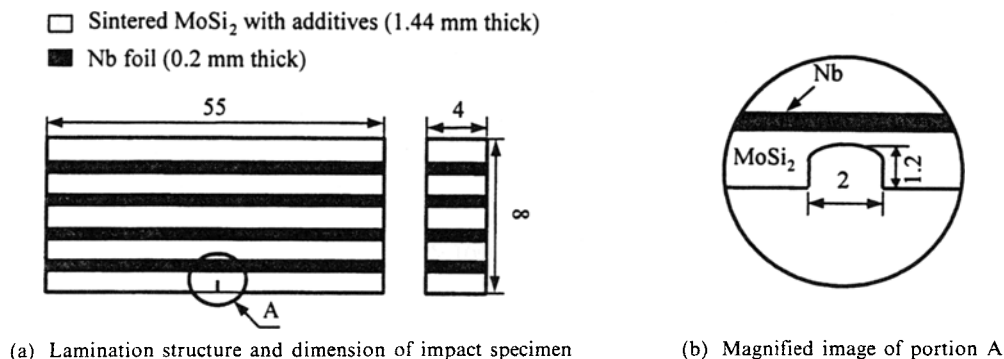


Fig. 1 Structure of laminate composites and dimension of the impact test specimen

impact test machine (Shimadzu HydrosHOT HMTM-1). Figure 1 shows the structure of laminate composites and the dimension of the impact test specimen. The U-shaped notch in the specimen was machined by electric discharge machining (EDM). The impact test was carried out on the flat wise specimen, in which impact load was normal to the lamination. The impact velocity and the span length were 3.3m/sec and 40mm, respectively.

An EPMA-WDS was used to compare the microstructure and the chemical composition of the interface between the matrix and the Nb foil. X-ray diffraction (XRD) analysis was also carried out to identify phases in MoSi₂ and MoSi₂-ZrO₂ materials consolidated at 1350°C.

4. Results and Discussion

4.1 Densities of laminate composites

The relative density of laminate composites was expressed as the ratio of the experimental density determined by Archimedes' method and the theoretical density calculated by the rule of mixture. The effect of the reaction layer on the density of laminate composites was also ignored in this study, because there is no any vacancy in the reaction layer. The relative densities of Nb/MoSi₂-SiC, Nb/MoSi₂-NbSi₂ and Nb/MoSi₂-ZrO₂ laminate composites were 91%, 91% and 94%, respectively. In the case of Nb/MoSi₂ to which no any kinds of particles were added, the density was 91%. The addition of ZrO₂ particle increased the density of Nb/MoSi₂. The relatively lower density of Nb/MoSi₂ without added particles was due to the use of raw MoSi₂ particles of large size and a low sintering temperature. (Rawers and Perry, 1996) When SiC or NbSi₂ particles having a size similar to that of MoSi₂ particles were added, there were no resulting changes in the density of Nb/MoSi₂. However, once ZrO₂ particle was added, since the particle size was very small to the extent of filling up voids occurred at the sintering process of MoSi₂, the density of Nb/MoSi₂-ZrO₂ was increased. Therefore, ZrO₂ particles of smaller size can be used effectively to improve the sintered density of Nb/MoSi₂.

4.2 Interfacial microstructures of laminate composites

Figure 2 represents interfacial regions of Nb/MoSi₂ and Nb/MoSi₂-ZrO₂ laminate composites. The volume fraction of ZrO₂ particle was 20%. The reaction layers of Nb/MoSi₂ were composed of (Nb, Mo)Si₂ and Nb₅Si₃. In contrast, the interfacial microstructure of Nb/MoSi₂ was changed by the addition of ZrO₂ particle. Only the Nb₅Si₃ phase was determined in the interfacial region of Nb/MoSi₂-ZrO₂, without (Nb, Mo)Si₂. The ZrSiO₄ phase was also identified in MoSi₂-ZrO₂ near the interfacial region. WDS line analyses of the interfacial regions (the black lines on the SEM micrographs in Fig. 2) shown in Fig. 3 indicate that the addition of ZrO₂ particle decreases the diffusion length of Si in the interface region of Nb/MoSi₂. This is because the reactivity of the Si element with Nb was suppressed by the formation of ZrSiO₄ in the MoSi₂-ZrO₂. A part of the MoSi₂ phase is transformed into the Mo₅Si₃ phase, after the reaction of ZrO₂ or Nb with Si. The ZrSiO₄ phase in the MoSi₂-ZrO₂ was confirmed by WDS quantitative analysis and XRD analysis. The Mo₅Si₃ phase by the reaction of MoSi₂ and ZrO₂ was also revealed by WDS quantitative analysis.

The effects of additive materials and ZrO₂ volume fractions on the thickness of the interfacial reaction layer in Nb/MoSi₂ laminate composites are shown in Table 1. From the results of the EPMA-WDS line analysis, the thickness of the reaction layer was defined as that region in which the composition of Nb was between 0 and 100%. From Table 1, the thickness of the reaction layer in Nb/MoSi₂ was not affected by the addition of SiC or NbSi₂ particles, whereas the addition of ZrO₂ decreased the reaction layer from 20μm to 11μm. Moreover, the reaction layer of Nb/MoSi₂ decreased with the increase of ZrO₂ volume fraction. These results indicate that addition of ZrO₂ is extremely effective for controlling the interfacial reaction of Nb/MoSi₂, as demonstrated by the calculation of the free energy change (see Sec. 2).

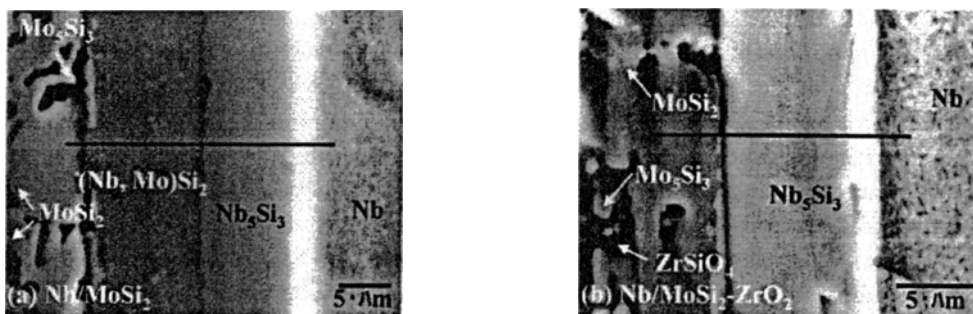
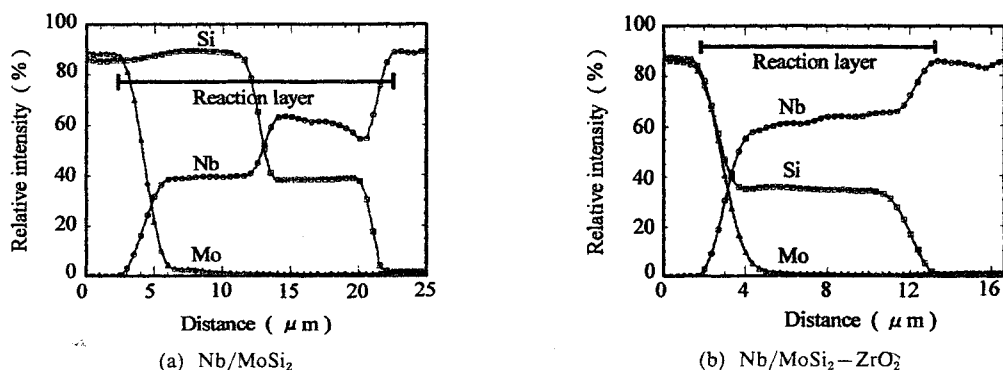

 Fig. 2 SEM micrographs of interfacial regions of Nb/MoSi₂ and Nb/MoSi₂-ZrO₂ laminates


Fig. 3 EPMA-WDS line analyses on the black lines represented in Fig. 2

 Table 1 The thickness of the interfacial reaction layer and the impact properties of Nb/MoSi₂ laminate composites containing SiC, NbSi₂ and ZrO₂ particles

| Materials | Additive material | Volume fraction of additive material (%) | Thickness of reaction layer (μm) | Impact load (N) | Fracture displacement (mm) | Crack initiation energy (J) | Crack propagation energy (J) |
|---|-------------------|--|----------------------------------|-----------------|----------------------------|-----------------------------|------------------------------|
| Nb/MoSi ₂ | - | - | 20.0 | 472.4 | 1.87 | 0.9 | 2.38 |
| Nb/MoSi ₂ -SiC | SiC | 20 | 19.0 | 472.1 | 2.00 | 1.05 | 2.66 |
| Nb/MoSi ₂ -NbSi ₂ | NbSi ₂ | 20 | 18.0 | 476.9 | 2.04 | 1.24 | 3.10 |
| Nb/MoSi ₂ -ZrO ₂ | ZrO ₂ | 10 | 13.5 | 473.3 | 2.33 | 1.10 | 3.42 |
| | | 20 | 11.0 | 482.2 | 3.02 | 1.19 | 6.45 |
| | | 30 | 9.0 | 493.9 | 2.35 | 1.20 | 3.90 |

4.3 Impact properties of laminate composites

4.3.1 Effects of addition of ZrO₂, SiC and NbSi₂

Impact properties of Nb/MoSi₂ laminate composites containing SiC, NbSi₂ or ZrO₂ particles are shown in Table 1. The absorbed impact energy is divided into the crack initiation energy

and the crack propagation energy. The former corresponds to the area under the impact load-displacement curve till the maximum load and the latter refers to this area after the maximum load. The maximum impact load of Nb/MoSi₂ did not depend on the addition of ZrO₂, SiC or NbSi₂ particles. However, the fracture displacement of Nb/MoSi₂ remarkably increased from (1.87mm) to 3.02mm after the addition of 20vol%

ZrO₂ particle, whereas the addition of SiC or NbSi₂ particles did not influence the fracture displacement. In addition, the crack initiation energy remains at a similar level regardless of the type of additive material, whereas the crack propagation energy depends on the additive materials. The addition of ZrO₂ particle significantly increased the crack propagation energy of Nb/MoSi₂, as a result of the increase in the fracture displacement. This can be explained from the viewpoint of the thickness of the reaction layer. The addition of ZrO₂ reduces the thickness of the reaction layer of Nb/MoSi₂, and then improves its crack propagation energy. Such a large improvement of the crack propagation energy will result from the increase in the plastic deformation of Nb foil accompanied with the decrease in the reaction layer, since the growth of the reaction layer strengthens the bonding between the matrix and Nb and restricts the deformation of Nb foil. The effect of the thickness of the reaction layer on the Charpy impact value of Nb/MoSi₂ laminate composites is shown in Fig. 4. The thickness of reaction layer depends on the material added, i.e., SiC, NbSi₂ or ZrO₂. The volume fraction of additive particle in matrix was fixed at 20vol%. It was found that the addition of SiC, NbSi₂ and ZrO₂ particles enhanced the impact value of Nb/MoSi₂, accompanied by a reduction of the reaction layer. In particular, the addition of ZrO₂ led to a remarkable increase in the impact value of Nb/MoSi₂. In detail illustration, the impact value of Nb/MoSi₂ containing ZrO₂ was 26.5kJ/m², about twice the value (11.8kJ/m²) for Nb/MoSi₂. Therefore, the addition of ZrO₂ particle is desirable to improve the impact properties of Nb/MoSi₂ associated with the suppression of the interfacial reaction.

4.3.2 Effect of ZrO₂ volume fraction

As seen in Table 1, the maximum impact load of Nb/MoSi₂ displays a gradual increase with an increasing volume fraction of ZrO₂ particle. However, the fracture displacement tends to decrease when the volume fraction become higher than 20vol %, even though the thickness of the reaction layer decreases successively. The decrease of the

fracture displacement directly leads to the reduction in the crack propagation energy of Nb/MoSi₂. The influence of the ZrO₂ volume fraction on the impact value of Nb/MoSi₂ is shown in Fig. 5. The impact value of Nb/MoSi₂ linearly increases with the addition of ZrO₂ particle, but results in a drastic reduction when ZrO₂ is higher than 20vol %. Such a result seems to be inconsistent with the relationship between the reaction layer and the impact value. This probably concerns the dispersion of ZrO₂ in MoSi₂. In the fabricating process of MoSi₂-ZrO₂ mixture, ZrO₂ particle showed a tendency to agglomerate when present at 30vol%. The impact value of MoSi₂-ZrO₂ material containing ZrO₂ particle of 30vol% was 2.6kJ/m² due to the reduction of the fracture

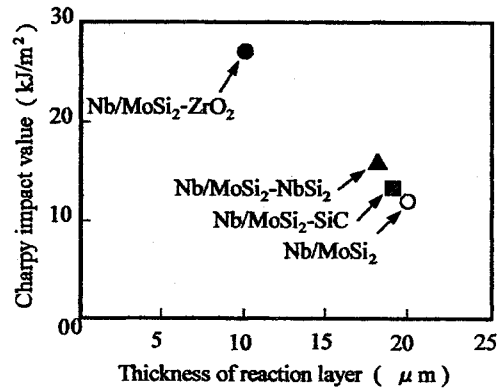


Fig. 4 Impact value and reaction layer thickness of Nb/MoSi₂ laminates depending on the addition of SiC, NbSi₂ and ZrO₂ particles

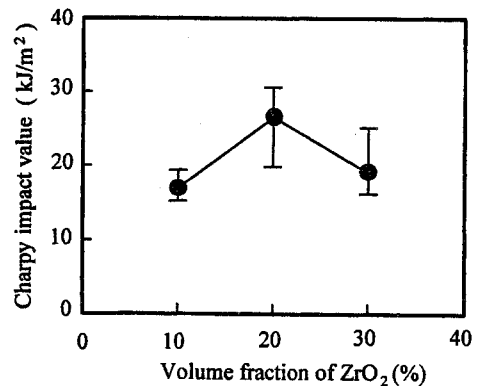


Fig. 5 Effect of ZrO₂ volume fraction on the impact value of Nb/MoSi₂ laminates

displacement, compared to that of 20vol% content (3.8kJ/m²). The inhomogeneous dispersion of ZrO₂ leads to a decrease in the impact value of laminate composites, together with a reduction in the toughness of matrix materials.

5. Summary

The interfacial reaction and impact properties of Nb/MoSi₂ laminate composites containing SiC, NbSi₂ and ZrO₂ particles have been evaluated. The sintered density of Nb/MoSi₂ laminate composites increased with the addition of ZrO₂ particle, comparing to those of SiC and NbSi₂ particles. Such an increase of density led to an improvement in the maximum impact load of Nb/MoSi₂ laminate composites. The thickness of the interfacial reaction layer of Nb/MoSi₂ laminate composites significantly reduced with the addition of ZrO₂ particle and the increase of ZrO₂ volume fraction. This is because Si tends to react with ZrO₂ to form ZrSiO₄ instead of reacting with Nb foil. Moreover, the addition of ZrO₂ particle into MoSi₂ phase obviously improved the impact value of Nb/MoSi₂ laminate composites due to the increase of the crack propagation energy, which resulted from the reduction of the interfacial reaction layer accompanying with the large plastic deformation of Nb foil. Therefore, ZrO₂ particle can be selected as an effective material to improve impact properties of Nb/MoSi₂ laminate composites through the suppression of the interfacial reaction.

References

Choi, N. S., and Kinloch, A. J., 1998, "Delamination Behavior of Multidirectional Laminate under the Mode I Loading," *Trans. KSME, A.*, Vol. 22, No. 3, pp. 611~623.

Kajuch, J., Short, J. and Lewandowski, J. J., 1995, "Deformation and Fracture Behavior of Nb in Nb₅Si₃/Nb Laminates and Its Effect on Laminate Toughness," *Acta Metall. Mater.*, Vol. 43,

pp. 1955~1967.

Lee, S. P., Sasaki, G. and Fukunaga, H., 1998, "Effect of Fabricating Conditions on Impact Properties of Nb/MoSi₂ Laminate Composites," *Journal of the Japan Institute of Metals*, Vol. 62, pp. 351~357.

Lu, T. C., Evans A. G., and Mehrabian, R., 1991, "Toughening of MoSi₂ with a Ductile (Niobium) Reinforcement," *Acta Metallurgica and Materialia*, Vol. 39, No. 8, pp. 1853~1862.

Meschter, P. J., and Schwartz, D. S., 1989, "Silicide-Matrix Materials for High-Temperature Applications," *Journal of Metal*, Vol. 41, No. 11, pp. 52~55.

Petrovic, J. J., Honnell, R. E., and Vasudevan, A. K., 1990, "SiC Reinforced-MoSi₂ Alloy Matrix Composites," *Material Research Society Symposium Proceedings*, Vol. 194, pp. 123~130.

Rawers, J. and Perry, K., 1996, "Crack Initiation in Laminated Metal-Intermetallic Composites," *Mater. Sci.*, Vol. 31, pp. 3501~3506.

Shah, D. M., Berezik, D., Anton D. L., and Hecht, R., 1992, "Appraisal of Other Silicides as Structural Materials," *Materials Science and Engineering*, Vol. A155, pp. 45~57.

Vasudevan, A. K., and Petrovic, J. J., 1992, "A Comparative Overview of Molybdenum Disilicide Composites," *Materials Science and Engineering*, Vol. A155, pp. 1~17.

Ward, C. H., and Culbertson, A. S., 1994, "Issues in Potential IMC Application for Aerospace Structures," *Material Research Society Symposium Proceedings*, Vol. 350, pp. 3~11.

Xiao, L. and Abbaschian, R., 1992, "Role of Matrix/Reinforcement Interfaces in the Fracture Toughness of Brittle Materials Toughened by Ductile Reinforcements," *Metall. Mater. Trans.*, Vol. 23A, pp. 2863~2872.

Yoon, H. K., Jeong, H. Y., Park, W. J., and Hue, J. W., 1995, "The Behavior of Crack Growth Rate for APAL and CPAL Patched with FRP Laminate in Aluminum Alloy Plate," *Trans. KSME, A.*, Vol. 19, No. 4, pp. 1013~1022.