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

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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.

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2. Thermodynamical Prediction of Interfacial Reaction

In the previous work, two distinct reaction layers, $(Nb, Mo)Si_2$ and Nb_5Si_3, were identified in the interfacial region of $Nb/MoSi_2$ laminate composites fabricated at 1350℃ . (Lee et at., 1998) Based on these results, the chemical reaction between Nb and $MoSi_2$ was shown as follows:

$$35MoSi_2 + 35Nb \rightarrow 20NbSi_2 + 7Mo_5Si_3 + 3Nb_5Si_3 \quad (1)$$
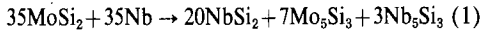
In this equation, the $(Nb, Mo)Si_2$ phase is assumed to approximate $NbSi_2$, because the former contains a small amount of Mo element (about 2 at %). The strong chemical behavior of Si to form silicides results in the growth of the interfacial reaction layer. Therefore, the interfacial reaction between Nb and $MoSi_2$ may be controlled by the suppression of Si diffusion from the $MoSi_2$ phase to the Nb phase. The addition of ZrO_2 particles into $MoSi_2$ is thermodynamically expected to reduce the interfacial reaction of $Nb/MoSi_2$. If Si element is isolated from $MoSi_2$, ZrO_2 particles in $MoSi_2$ tend to form the $ZrSiO_4$ phase before reacting with Nb. Consequently, the diffusion of Si element can be decreased relative to that in $Nb/MoSi_2$. From this concept, the interfacial reaction (1) of $Nb/MoSi_2$ is transformed into the reaction (2) by the addition of ZrO_2. The $ZrSi_2$ phase will be formed as a product of the reaction (2). Furthermore, the $NbSi_2$ phase in the reaction (1) vanishes at the interface of $Nb/MoSi_2$-ZrO_2.

$$15MoSi_2 + 8ZrO_2 + 15Nb \rightarrow 4ZrSiO_4$$
$$+ 3Mo_5Si_3 + 3Nb_5Si_3 + 4ZrSi_2 \quad (2)$$
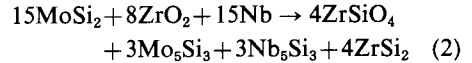
Standard free energy changes for reactions (1) and (2) calculated at 1350℃ are -1.73×10^6 (J/mol) and -4.59×10^5 (J/mol), respectively. The resulting free energies will have negative values, and interfacial reactions will therefore be possible. These thermodynamical results demonstrate that the addition of ZrO_2 particles into $MoSi_2$ can decrease the thickness of the reaction layer in $Nb/MoSi_2$.

3. Experimental Procedures

The four matrices used in this experiment were $MoSi_2$, $MoSi_2$-$NbSi_2$, $MoSi_2$-SiC and $MoSi_2$-ZrO_2. The sizes of $MoSi_2$, $NbSi_2$, SiC and ZrO_2 particles were 2.8μm, 3.5μm, 3.0μm and 0.1μm, 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 $NbSi_2$ and SiC particles dispersed in $MoSi_2$ powder was held to 20vol %. The volume fraction of ZrO_2 (containing 5.14wt% Y_2O_3) particle was varied from 10vol % to 30vol %. All laminate composites were fabricated successfully by vacuum hot pressing for 3.6 ks at 1350℃ 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

☐ Sintered $MoSi_2$ with additives (1.44 mm thick)
■ Nb foil (0.2 mm thick)
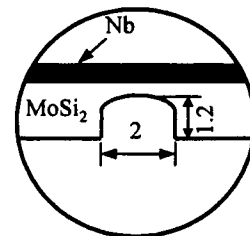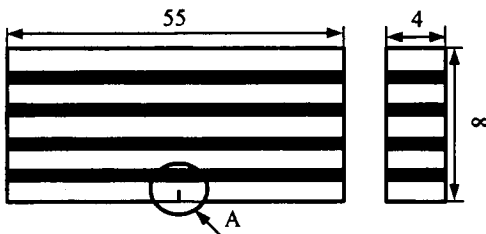
(a) Lamination structure and dimension of impact specimen   (b) Magnified image of portion A

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

impact test machine (Shimadzu Hydroshot HTM -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 $MoSi_2$ and $MoSi_2$ -ZrO_2 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 $Nb/MoSi_2$ -SiC, $Nb/MoSi_2$-$NbSi_2$ and $Nb/MoSi_2$-ZrO_2 laminate composites were 91%, 91% and 94%, respectively. In the case of $Nb/MoSi_2$ to which no any kinds of particles were added, the density was 91 %. The addition of ZrO_2 particle increased the density of $Nb/MoSi_2$. The relatively lower density of $Nb/MoSi_2$ without added particles was due to the use of raw $MoSi_2$ particles of large size and a low sintering temperature. (Rawers and Perry, 1996) When SiC or $NbSi_2$ particles having a size similar to that of $MoSi_2$ particles were added, there were no resulting changes in the density of $Nb/MoSi_2$. However, once ZrO_2 particle was added, since the particle size was very small to the extent of filling up voids occurred at the sintering process of $MoSi_2$, the density of $Nb/MoSi_2$-ZrO_2 was increased. Therefore, ZrO_2 particles of smaller size can be used effectively to improve the sintered density of $Nb/MoSi_2$.

4.2 Interfacial microstructures of laminate composites

Figure 2 represents interfacial regions of $Nb/$ $MoSi2$ and $Nb/MoSi_2$-ZrO_2 laminate composites. The volume fraction of ZrO_2 particle was 20%. The reaction layers of $Nb/MoSi_2$ were composed of $(Nb, Mo)Si_2$ and Nb_5Si_3. In contrast, the interfacial microstructure of $Nb/MoSi_2$ was changed by the addition of ZrO_2 particle. Only the Nb_5Si_3 phase was determined in the interfacial region of $Nb/MoSi_2$-ZrO_2, without $(Nb, Mo)Si_2$. The $ZrSiO_4$ phase was also identified in $MoSi_2$-ZrO_2 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 ZrO_2 particle decreases the diffusion length of Si in the interface region of $Nb/MoSi_2$. This is because the reactivity of the Si element with Nb was suppressed by the formation of $ZrSiO_4$ in the $MoSi_2$-ZrO_2. A part of the $MoSi_2$ phase is transformed into the Mo_5Si_3 phase, after the reaction of ZrO_2 or Nb with Si. The $ZrSiO_4$ phase in the $MoSi_2$-ZrO_2 was confirmed by WDS quantitative analysis and XRD analysis. The Mo_5Si_3 phase by the reaction of $MoSi_2$ and ZrO_2 was also revealed by WDS quantitative analysis.

The effects of additive materials and ZrO_2 volume fractions on the thickness of the interfacial reaction layer in $Nb/MoSi_2$ 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 $Nb/MoSi_2$ was not affected by the addition of SiC or $NbSi_2$ particles, whereas the addition of ZrO_2 decreased the reaction layer from 20μm to 11μm. Moreover, the reaction layer of $Nb/MoSi_2$ decreased with the increase of ZrO_2 volume fraction. These results indicate that addition of ZrO_2 is extremely effective for controlling the interfacial reaction of $Nb/MoSi_2$, as demonstrated by the calculation of the free energy change (see Sec. 2).
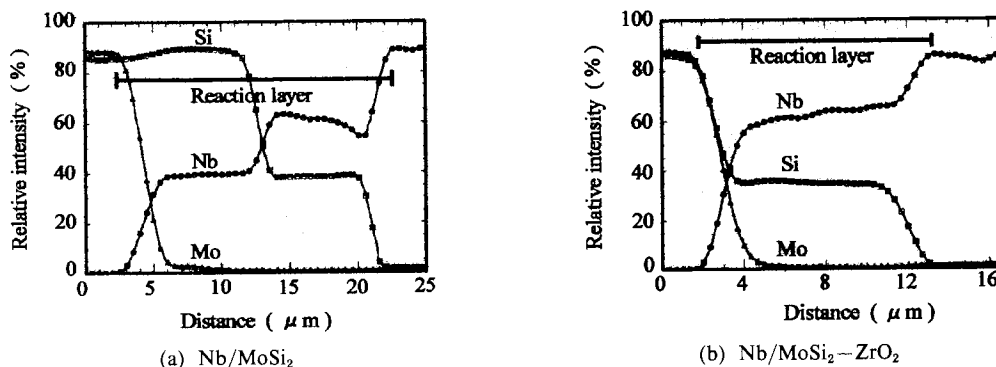
Fig. 2 SEM micrographs of interfacial regions of $Nb/MoSi_2$ and $Nb/MoSi_2-ZrO_2$ laminates

(a) $Nb/MoSi_2$ (b) $Nb/MoSi_2-ZrO_2$

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
$Nb/MoSi_2$ laminate composites containing SiC, $NbSi_2$ and ZrO_2 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
$Nb/MoSi2-NbSi_2$	$NbSi_2$	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 ZrO_2, SiC and $NbSi_2$

Impact properties of $Nb/MoSi_2$ laminate composites containing SiC, $NbSi_2$ or ZrO_2 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 $Nb/MoSi_2$ did not depend on the addition of ZrO_2, SiC or $NbSi_2$ particles. However, the fracture displacement of $Nb/MoSi_2$ remarkably increased from (1. 87mm) to 3.02mm after the addition of 20vol%

ZrO_2 particle, whereas the addition of SiC or $NbSi_2$ 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 ZrO_2 particle significantly increased the crack propagation energy of $Nb/MoSi_2$, 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 ZrO_2 reduces the thickness of the reaction layer of $Nb/MoSi_2$, 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 $Nb/MoSi_2$ 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, $NbSi_2$ and ZrO_2 particles enhanced the impact value of $Nb/MoSi_2$, accompanied by a reduction of the reaction layer. In particular, the addition of ZrO_2 led to a remarkable increase in the impact value of $Nb/MoSi_2$. In detail illustration, the impact value of $Nb/MoSi_2$ containing ZrO_2 was $26.5kJ/m^2$, about twice the value ($11.8kJ/m^2$) for $Nb/MoSi_2$. Therefore, the addition of ZrO_2 particle is desirable to improve the impact properties of $Nb/MoSi_2$ associated with the suppression of the interfacial reaction.

4.3.2 Effect of ZrO_2 volume fraction

As seen in Table 1, the maximum impact load of $Nb/MoSi_2$ displays a gradual increase with an increasing volume fraction of ZrO_2 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 $Nb/MoSi_2$. The influence of the ZrO_2 volume fraction on the impact value of $Nb/MoSi_2$ is shown in Fig. 5. The impact value of $Nb/MoSi_2$ linearly increases with the addition of ZrO_2 particle, but results in a drastic reduction when ZrO_2 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 ZrO_2 in $MoSi_2$. In the fabricating process of $MoSi_2$-ZrO_2 mixture, ZrO_2 particle showed a tendency to agglomerate when present at 30vol%. The impact value of $MoSi_2$-ZrO_2 material containing ZrO_2 particle of 30vol% was $2.6kJ/m^2$ due to the reduction of the fracture
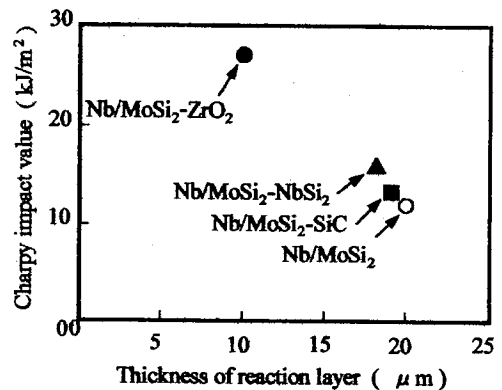

Fig. 4 Impact value and reaction layer thickness of $Nb/MoSi_2$ laminates depending on the addition of SiC, $NbSi_2$ and ZrO_2 particles
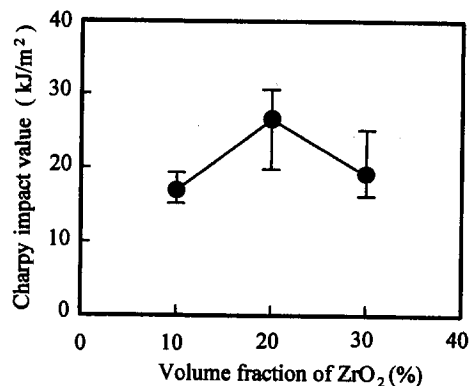

Fig. 5 Effect of ZrO_2 volume fraction on the impact value of $Nb/MoSi_2$ laminates

displacement, compared to that of 20vol% content ($3.8kJ/m^2$). The inhomogeneous dispersion of ZrO_2 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 $Nb/MoSi_2$ laminate composites containing SiC, $NbSi_2$ and ZrO_2 particles have been evaluated. The sintered density of $Nb/MoSi_2$ laminate composites increased with the addition of ZrO_2 particle, comparing to those of SiC and $NbSi_2$ particles. Such an increase of density led to an improvement in the maximum impact load of $Nb/MoSi_2$ laminate composites. The thickness of the interfacial reaction layer of $Nb/MoSi_2$ laminate composites significantly reduced with the addition of ZrO_2 particle and the increase of ZrO_2 volume fraction. This is because Si tends to react with ZrO_2 to form $ZrSiO_4$ instead of reacting with Nb foil. Moreover, the addition of ZrO_2 particle into $MoSi_2$ phase obviously improved the impact value of $Nb/MoSi_2$ 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, ZrO_2 particle can be selected as an effective material to improve impact properties of $Nb/MoSi_2$ laminate composites through the suppression of the interfacial reaction.

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