MECHANICAL PROPERTIES OF NiAl-TiB₂ COMPOSITE MATERIALS

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ABSTRACT

Composite materials of nickel aluminide and titanium diboride were fabricated using spark plasma sintering at 1573K. Composition dependence of the bending strength, Vickers hardness and the indentation fracture toughness were investigated. The bending strength of NiAl increased rapidly with the addition of TiB₂ up to 20vol% and decreased gradually by the further addition. This composition dependence of the bending strength was explained on the basis of the strengthening mechanisms due to grain refining of the matrix phase and stress transfer from the matrix to the reinforcement particles. The Vickers hardness increased with the amount of TiB₂ and the highest value of 1600Hv was obtained for NiAl-78vol%TiB₂. By the SEM observation, indentation cracks were observed in the composites containing TiB₂ more than 56vol%. The fracture toughness of NiAl-56vol%TiB₂ was 22MPa·m⁰.⁵, which decreased to 15 MPa·m⁰.⁵ of NiAl-78vol%TiB₂. It is conjectured that the decrease of the fracture toughness is related with the decrease of the bending strength.

Keywords: TiB₂, NiAl, bending strength, Vickers hardness, fracture toughness.

INTRODUCTION

Titanium diboride (TiB₂) has many desirable properties such as high hardness (Hv=3400), high melting point (3000K), low density (4.50x10³kg/m³), high electrical resistivity and good corrosion resistance. It is a promising candidate for cutting tools, wear proof parts, aircraft propulsion systems, space vehicle thermal protection and so on. Attempts have been made to consolidate TiB₂ powders into dense solid bodies by reaction sintering and hot pressing. However, a high sintering temperature above 2000K is required to obtain dense TiB₂ bulk samples (Wang, 2002). Grain growth proceeds by the sintering at such high temperature and mechanical properties such as bending strength deteriorates, which limits its application.

The intermetallic compound NiAl has a number of favorable properties such as high melting temperature (1800K), low density (5.86x10³kg/m³) and excellent oxidation resistance. It has been shown that the addition of TiB₂ to NiAl up to 30vol% significantly improves the compressive strength of NiAl (Whittenberger, 1990). In the previous study we have shown that dense NiAl-TiB₂ composites can be obtained for the amount of TiB₂ up to 67vol% by the spark plasma sintering at 1573K (Yoshida, 2014). The Vickers hardness is found to increase with the amount of TiB₂ and the highest value of 1600Hv has been obtained for NiAl-67vol%TiB₂. The bending strength of TiB₂-NiAl composites increases rapidly by the addition of TiB₂ up to 20vol% and decreases gradually by the further addition.
In the particle reinforced composites, several damage modes such as cracking of the reinforcements and particle/matrix interface decohesion may develop by loading. These damage modes affect the mechanical performance of the composite (Maire, 1997). In the present study we have investigated the composition dependence of the bending strength, Vickers hardness and the indentation fracture toughness of NiAl-TiB₂ composites. The composition dependence of the bending strength and the fracture toughness of NiAl-TiB₂ composite have been analysed based on a numerical model.

EXPERIMENTAL METHOD

The raw materials were commercially available TiB₂ powders of 99.9% purity, Al powders of 99.9% purity and Ni powders of 99.9% purity (all powders by Furuuchi Chemical Corp.). The diameter of TiB₂ powder particles was a few microns and those of Al and Ni powders were around 10 microns. Nickel aluminide containing between 45 at% and 57 at% Ni forms B₂ structure based on the body centered cubic lattice (Miracle, 1993). In the present study, the ratio of Ni in NiAl is fixed to 55 at%.

A graphite die, having an internal diameter of 20mm and a wall thickness of 10mm was filled with 5x10⁻³kg of the mixed powders of NiAl-TiB₂, sealed by two graphite punches and mounted on the equipment, LABOX625 fabricated by Sinterland Ltd. The mixed powders were heated to 1573K with the rate of 50K/min, kept for 10 minutes, and then furnace cooled to room temperature. Temperature was measured using the infrared radiation thermometer IR-AHS0 fabricated by Chino Corp. Sintering was performed in a vacuum with a residual pressure of 10Pa. A uniaxial pressure of 20MPa was applied during the sintering. SEM observation was performed using a Hitachi H-4300 instrument. X-ray diffraction patterns were measured using X-ray diffractometer ULTIMA IV fabricated by Rigaku with Cu-kα radiation source. Vickers hardness was measured using an Akashi AVK-A hardness tester with the load of 490N and pressing time of 15 seconds. To perform the bending test, rectangular shape samples with the size of 2x3x20 mm³ were cut by the electric discharge. Three points bending tests were performed using a Shimadzu AGS-J test machine with the crosshead speed of 0.5mm/min and the span of 15mm.

EXPERIMENTAL RESULTS

Figure 1 shows the X-ray diffraction pattern of the polished surface of NiAl, NiAl-25vol%TiB₂ and NiAl-67vol%TiB₂ specimens sintered at 1573K. In the X-ray diffraction patterns of NiAl, peaks from cubic B₂ type structure are observed. In the X-ray diffraction pattern of NiAl-TiB₂ composites, peaks from TiB₂ of hexagonal AlB₂ type structure indicated by arrows and from NiAl of cubic B₂ lattice structures have been observed. These results reveal that NiAl and TiB₂ exist in equilibrium at 1573K.

Figure 2 (a) shows the SEM image of the polished and etched surface of the sintered NiAl specimen. Etching has been performed by HNO₃ to reveal the grain boundaries. In Figure 2 (a) it has been shown that the grain size of NiAl is around 20 µm and, on the grain boundaries, some pores of several µm are formed as indicated by arrows. Figure 2 (b), (c) and (d) shows the SEM images of the polished surface of NiAl-25vol%TiB₂, NiAl-67vol%TiB₂ and monolithic TiB₂ specimens sintered at 1573K. In Figure 2 (b), it is found that NiAl fills the space among TiB₂ grains showing good wetting property of TiB₂ and NiAl. No pore is observed in NiAl-25vol%TiB₂ being different from the case of monolithic NiAl. The size of TiB₂ particle is several µm which is the same as that of the starting powders. In NiAl-
67vol%TiB$_2$ shown in Figure 3 (c) some pores are observed as indicated by arrows. The thermal expansion coefficients of TiB$_2$ is $9.3 \times 10^{-6}$ (K$^{-1}$) along the c-axis and $6.35 \times 10^{-6}$ (K$^{-1}$) along the a-axis (Okamoto, 2010) which are smaller than that of NiAl, $15.1 \times 10^{-6}$ K$^{-1}$ (Miracle, 1993). These pores may be caused by the thermal mismatch between NiAl and TiB$_2$. In Figure 2 (d), it is found that TiB$_2$ specimen sintered at 1573K is granular showing that sintering of TiB$_2$ does not proceed well at 1573K.

In Figure 3 is shown the composition dependence of the bending strength of NiAl-TiB$_2$ composites. The bending strength of NiAl sintered at 1573K is 380MPa, which increases rapidly as the amount of TiB$_2$ increases up to 20vol% and the highest value of 990MPa is obtained. The bending strength decreases gradually as the amount of TiB$_2$ increases above 20vol%. The bending strength of monolithic TiB$_2$ sintered at 1573K is as low as 200MPa. The dependence of the bending strength on the volume fraction of TiB$_2$ will be discussed in the next section.

In Figure 4 is plotted the Vickers hardness of NiAl-TiB$_2$ composites indented at the load of 490N. The Vickers hardness of monolithic NiAl is 350 Hv, which increases as the amount of TiB$_2$ increases. The Hv value of the NiAl-78vol%TiB$_2$ is as high as 1600 Hv. The Hv value of monolithic TiB$_2$ sintered at 1573K is as low as 750Hv. These results are similar to those indented at the load of 2N reported in the previous paper (Yoshida, 2014).

Figure 5 shows the SEM images of the Vickers indentation of NiAl-25vol%TiB$_2$ indented at the load of 490N. Cracking occurs along the edge of the indentation. In Fig. 6 (a) and (b) shows the SEM images of the Vickers indentation of NiAl-57vol%TiB$_2$ indented at the load of 490N. In Fig. 6 (a), indentation cracks are observed to emanate from the indentation corners. Figure 6 (b) is the expanded image of the region encircled in Figure 6 (a). A crack is observed to propagate in the NiAl matrix and/or along the interface between TiB$_2$ particle and NiAl matrix and is terminated at the surface of a TiB$_2$ particle, suggesting that a TiB$_2$ particle has an effect to stop the crack propagation.

Figures 7 and 8 show the Vickers indentation of NiAl-67vol%TiB$_2$ and NiAl-78vol%TiB$_2$, respectively. In both specimens, cracks are observed to emanate from indentation corners. The crack length is longer for NiAl-78vol%TiB$_2$ than NiAl-67vol%TiB$_2$ specimens indicating poorer fracture toughness of the former than the latter.

Various models to deal with the indentation fracture have been proposed which have been reviewed by Ponton and Rawlings. (Ponton, 1989) The indentation fracture models are classified into two groups, in one group it is assumed that the cracks which form as a result of Vickers indentation are well developed radial-media halfpenny-shaped cracks, and in the other group it is assumed that radial Palmqvist cracks are formed. The empirical criterion for the halfpenny cracks is the ratio $c/a$ larger than 2 where $a$ is half length of the indentation diagonal and $c$ the crack length measured from the indentation center. In the present experiment, all cracks are seemed to be Palmqvist type.

For the Palmqvist type cracks, the following equation is proposed to estimate the fracture toughness value $Kc$ as,

$$ K_c=0.0329P/\alpha t^{1/2} $$ (1),

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where $P$ is the indentation load, $a$ half length of the indentation diagonal and $l$ the crack length measured from the indentation corner (Ponton, 1989). The fracture toughness values obtained using eq. (1) are summarized in Table 1. The $K_c$ value of NiAl-56vol%TiB$_2$ is 22MPa·$m^{1/2}$, which decreases to 15 MPa·$m^{1/2}$ of NiAl-78vol%TiB$_2$.

![X-ray diffraction pattern](image)

**Fig. 1** - X-ray diffraction pattern from NiAl, NiAl-25vol%TiB$_2$ and NiAl-67vol%TiB$_2$.

![SEM images](image)

**Fig. 2** - SEM image of (a) NiAl, (b) NiAl-25vol%TiB$_2$, (c) NiAl-67vol%TiB$_2$ and (d) TiB$_2$ sintered at 1573K.
Fig. 3 - Dependence on the amount of TiB$_2$ of the bending strength of NiAl-TiB$_2$ composite

Fig. 4 - Dependence on the amount of TiB$_2$ of the Vickers hardness of NiAl-TiB$_2$ composite

Fig. 5 - SEM image of the Vickers indentation of NiAl-25vol%TiB$_2$ loaded at 490N
DISCUSSION

The bending strength of NiAl is found to increase by the addition of TiB$_2$ up to 20vol% and decrease gradually by the further addition. The fracture toughness is found to decrease as the volume fraction of TiB$_2$ increases above 56vol%. We consider below the dependence on the volume fraction of the bending strength and the fracture toughness of the NiAl-TiB$_2$ composites.

Reinforcement of particle-reinforced composites has been analyzed using mean field theory by Mori and Tanaka (Mori, 1973) based on the equivalent inclusion model contrived by Eshelby (Eshelby, 1957). By the Mori and Tanaka’s theory, mean stress in the matrix, $\sigma_m$, is expressed by external stress $\sigma_0$ of the composite as,

$$\sigma_m = \sigma_0 g(\phi)$$  \hspace{1cm} (2)

where function $g(\phi)$ is the normalized mean stress dependent on the elastic moduli of matrix and reinforcement. Normalized mean stress in the matrix, $\sigma_m/\sigma_0$ and in the reinforcement particles, $\sigma_r/\sigma_0$, calculated by using the Mori and Tanaka scheme is shown in Figure 9 as a function of the volume fraction of TiB$_2$. We assumed the spherical shape and isotropic elastic module of reinforcement. The used values of Young’s modulus and Poisson ratio of TiB$_2$ are 580GPa and 0.11 (Schulson, 1983), and those of NiAl are 200GPa and 0.30 (Miracle, 1993), respectively.

In Figure 9, it is shown that the normalized stress in the matrix, $\sigma_m/\sigma_0$, decreases as the volume fraction of the reinforcement, $\phi$, increases indicating that more stress is carried by the reinforcement particle. The stress in the matrix is expected to reduce about 10% when 20vol% TiB$_2$ is added to NiAl. If a failure of the composite occurs when the stress exceeding the ultimate tensile strength is applied to the matrix phase, $g(\phi)^{-1}$ gives the improvement of the strength of the composite relative to the monolithic matrix material. However, this effect is not sufficient to give about 250% improvement of the bending strength of NiAl-20volTiB$_2$ relative to that of monolithic NiAl shown in Figure 3. In order to describe the increment of the bending strength of NiAl-TiB$_2$ composite, another strengthening mechanism is needed.

Schulson and Barker have reported the Grain size dependence of the fracture strength of NiAl polycrystalline aggregates (Schulson, 1983). They have found that the tensile strength of NiAl increases depending on the reciprocal square root of grain size. The increment of the bending strength of NiAl-TiB$_2$ composites may be caused by the decrease of the grain size of NiAl by the addition of TiB$_2$. We consider the strengthening effect associated with the reduction of grain size of the matrix phase.

The average distance between the surfaces of the nearest particles in the composites, $<La>$, depends on the size and the amount of particles. $<La>$ has been calculated by Adachi et al as a function of volume fraction, $\phi$, and particle diameter, $D_m$, assuming sphere shape and uniform particle dispersion (Adachi, 2008). In Figure 10 is plotted the calculated result of $(<La>/D_m)^{-1/2}$. The distance $<La>$ at a volume fraction 0.055 was equal to the particle diameter $D_m$ and the shortest distance at $\phi=0.74$ (maximum volume fraction in the close packed structure) was 0.134$D_m$.

The strength of the NiAl-TiB$_2$ composites is expected to be given by the next equation.

$$\sigma_{\text{comp crit}}^\text{NiAl} = g(\phi)^{-1} <La>^{-1/2} \sigma_{\text{NiAl crit}}^\text{NiAl}$$  \hspace{1cm} (3)

In Figure 11 is plotted $(<La>/D_m)^{-1/2}$. Equation (3) gives an increasing curve as the volume fraction increases. As shown in Figure 3, the bending strength of NiAl increases by the addition of TiB$_2$ up to 20vol% and decreases gradually by the further addition. This increase of the bending strength may be explained by the strengthening mechanisms by grain refinement described above. However, it cannot explain the decrease of the bending strength above 20vol%.

By the SEM observation shown in Figure 2, each TiB$_2$ particle is isolated in the NiAl matrix in the NiAl-25vol%TiB$_2$ specimen. On the other hand, in the NiAl-67vol% TiB$_2$ specimen, almost all TiB$_2$ grains are in contact with other TiB$_2$ particles. Bonding strength between TiB$_2$ particles is weak as indicated by the fact that the bending strength of monolithic TiB$_2$ sintered
at 1573K is as low as 200MPa. The decrease of the bending strength of NiAl-TiB$_2$ composites as the amount of TiB$_2$ increase above 20vol% is seemed to be caused by the increase of the fractions of TiB$_2$ surfaces in contact with other TiB$_2$.

The fraction of the area of TiB$_2$ surfaces in contact with other TiB$_2$ can be given as (1-φ). Thus the strength is given as follows.

$$
\sigma_{\text{comp} \text{crit}} = (1-\phi) \ g(\phi)^{-1} \ (<\text{La}>/\text{Dm})^{-1/2} \ \sigma_{\text{NiAl} \text{crit}} 
$$

(4)

In Figure 11 is plotted (1-φ) g(φ)$^{-1}$ (<La>/Dm)$^{-1/2}$, also, as a function of the volume fraction. This curve has maximum at the volume fraction φ around 35%.

In Fig. 12 is plotted the composition dependence of $\sigma_{\text{comp} \text{crit}}$ given by eq. (4) and the experimental values of the bending strength of NiAl-TiB$_2$ composites where a coefficient is chosen so that $\sigma_{\text{comp} \text{crit}}$ and the experimental value are in accord at φ=0.2. It is seen in Fig. 12 that the bending strength of the composite is well fitted by eq. (4).

Fracture toughness provided by reinforcement by particles can also be evaluated similarly. It seems that, in NiAl-TiB$_2$ composites, both the fracture toughness and the bending strength decreases as the amount of TiB$_2$ increases above 56%. Fracture toughness is given as $\sigma_{\text{comp} \text{crit}} \cdot \rho^{1/2}$ where $\rho$ is the characteristic length representing the crack tip curvature or the plastic zone size at the crack tip. Fracture toughness is expected to have a similar volume fraction dependence as the bending strength assuming that the characteristic length $\rho$ does not depend on $\phi$. The characteristic length $\rho$ estimated by the bending strength and the fracture toughness values for NiAl-56vol%TiB$_2$ is around 300µm which is nearly the same as the size of the Vickers indentation. In NiAl no plastic deformation occurs at room temperature (Miracle, 1993). This may imply that deformation is caused by generating micro cracks in the entire indentation region.

![Normalized stress](image_url)
CONCLUSION

Composite materials of nickel aluminide and titanium diboride were fabricated using spark plasma sintering. The bending strength of NiAl-TiB₂ composites increased rapidly with the volume fraction of TiB₂ up to 20vol% and decreased gradually by the further addition. The
improvement of the bending strength was explained on the basis of the strengthening mechanisms due to grain refining of the matrix phase and stress transfer from the matrix to the reinforcement particles. The decrease of the bending strength above 20vol% was explained by the poor cohesion between TiB$_2$ particles. By the SEM observation, indentation cracks were observed in the composites containing TiB$_2$ more than 56vol%. The fracture toughness was found to decreases as the volume fraction of TiB$_2$ increases above 56vol%. It is conjectured that the decrease of the fracture toughness is related with the decrease of the bending strength.

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REFERENCES


