Microstructural analysis and mechanical properties of in situ Nb/Nb-aluminide layered materials

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1. Introduction

Intermetallic compound materials attracted interest as a substitute for superalloys and for various automotive components due to their lightweight, high elevated temperature strength and good creep resistance [1–7]. However, application of intermetallic compound materials has been limited due to brittleness at room temperature. In order to improve toughness, intermetallic compound matrix composites are currently being developed by incorporating ductile reinforcements with various shapes, e.g. particulate, fiber, tube or sheet [1–3,8]. Intermetallic compound composites are mainly manufactured by solidification, powder metallurgy or sputtering processes. However, solidification process has its shortcoming due to brittleness after manufacturing which makes it difficult for secondary machining. Although powder metallurgy or sputtering processes are adequate for manufacturing small functional material, the limit in chamber size makes it difficult to manufacture large structural material. Additional disadvantage arises from high cost for equipment and maintenance.

In order to be widely accepted for intermetallic composites as high-temperature structural material, development of a new manufacturing process is required, which should be simple and easy to operate, capable of manufacturing bulk near-net shape products at low cost and utilizing conventional equipment. Recently, hot press thin foil process has been developed for manufacturing metal/intermetallic compound laminate composites, which utilizes hot press to induce self-propagating high-temperature synthesis (SHS) reaction between different pure metal sheets. Hot press thin foil process is rather economical process in manufacturing metal/intermetallic compound laminate composites having layered thickness of several tenth to several hundredth μm. Fundamental research is being carried out particularly on Ti, Ni, Fe, Mo, Nb-based intermetallic compound composites and also ceramic composites [9–19].

The Nb–Al system intermetallic compounds have high potential for substituting Ni-based superalloys and Ni, Ti and Fe-based intermetallic compounds [20–27], due to high melting point, good tensile strength at elevated temperature and low densities of 4.5, 6.9 and 7.3 g/cm\textsuperscript{3} for NbAl\textsubscript{3}, Nb\textsubscript{2}Al and Nb\textsubscript{3}Al phases, respectively. The Nb–Al system intermetallic compounds are mainly produced either as monolithic NbAl\textsubscript{3} or Nb\textsubscript{2}Al intermetallic compounds by solidification [21–24], HIP [22], mechanical alloying [28] or CCE processes [29]. However, monolithic NbAl\textsubscript{3} or Nb\textsubscript{2}Al intermetallic compounds have low fracture...
toughness of 1–3 MPa m and difficulty in producing [30]. Therefore, various shapes of ductile reinforcements are incorporated into the Nb–Al system matrix in order to improve toughness and produce intermetallic compound composites [31–34]. Bloyer et al. [33,34] manufactured Nb/Nb₃Al laminate composite with layer thickness in several tenth to several hundredth µm using Nb sheets and Nb₃Al powders. The mechanical properties showed improvement in both toughness and fatigue properties compared with Nb dispersed or Nb/Nb₃Al laminate composite of layer thickness in 1–2 µm. Recently, Chung et al. [35] manufactured Nb/Nb-based intermetallic compound laminate composite with layer thickness in several tenth to several hundredth µm using pure metal sheets and investigated the formation of the intermetallic compound layer.

Based on the manufacturing process of Nb–Al system laminate composite reported by Chung et al. [35], modification on the formation of intermetallic compound phases was made by changing the heat treatment during the vacuum synthesis. Investigation on the relationship between the processing conditions and the resulting microstructure, the formation sequence of intermetallic compound phases and mechanical properties of the laminate composite were carried out.

2. Experimental procedure

The manufacturing process of the Nb–Al system laminate composites is described elsewhere [35]. In order to produce different types of phases in the intermetallic layer, three different vacuum synthesis conditions were carried out, termed P1, P2 and P3. P2 condition was processed to compare the structural difference with P1 and P3 conditions. Fig. 1 shows the schematic diagram of the synthesis temperature and applied pressure for each condition. Table 1 summarizes Al and Nb sheets thickness for each condition and the resulting intermetallic phases after each synthesis.

For microstructural analysis, X-ray and compositional analysis samples were prepared by grinding and polishing with diamond suspension. Microstructural analysis was carried out using optical microscopy (Leco-300) and SEM (Hitachi S-4200). In order to identify the phases formed in the samples, X-ray analysis (Rigaku PMAX-3C) was carried out.

Table 1

| Sheet thickness (mm) | Heat treatment | Pressure (MPa) | Intermetallic phases                  |
|----------------------|----------------|---------------|--------------------------------------|
| Nb                   | Al             |               |                                      |
| P1 0.1 0.07          | 933 K × 2 h → 1023 K × 0.1 h → 1173 K × 10 h → 1723 K × 2 h | 30 | Nb, Nb₃Al, Nb₂Al, Nb₃Al₃ (weak) |
| P2 0.1 0.05          | 933 K × 2 h → 1023 K × 0.1 h → 1173 K × 10 h → 1473 K × 2 h | 30 | Nb, Nb₂Al (strong), Nb₃Al₃ (weak) |
| P3 0.1 0.1           | 933 K × 2 h → 1023 K × 0.1 h → 1673 K × 2 h | 30 | Nb, Nb₂Al (weak), Nb₃Al₃ (strong) |
out using monochromatic Cu Kα from 20 to 90° with 4°/min scanning speed.

Compositional variation within the layer and at the interlayer was analyzed by spot and line analysis using energy dispersive X-ray spectroscopy (EDS, Horiba Super Xephry, EMAX-5770) attached to SEM. In order to investigate the phase distribution in the intermetallic layer microvickers hardness test was carried out under 300 g load and loading time of 30 s. For mechanical properties of the samples produced by P1 and P3 processes, tensile test was carried out using with samples 50 mm in length, 2.6 and 4.2 mm in thickness for P3 and P1, respectively and 20 mm in parallel length. The fractured surface of the sample was further examined by SEM. Three point bending test was carried out to measure the fracture toughness of the samples. Each test was performed using Instron machine (Instron 4482), with loading velocity of 0.1 mm/min.

The stress expansion coefficient was calculated using Eqs. (1) and (2)

\[
K = \frac{PSf(\alpha)}{BW^{3/2}}
\]

where \( P \) is the load, \( S \), the span length, \( W \), the width of the sample, \( B \), the thickness of the sample and \( f(\alpha) \) is the shape factor, given by Eq. (2)

\[
f(\alpha) = 3\alpha^{1/2}[1.99 - \alpha(1 - \alpha)(2.15 - 3.93\alpha + 2.7\alpha^2)]
\]

\[
\times 2(1 + 2\alpha)(1 - \alpha)^{3/2}
\]

where \( a \) is the notch length and \( \alpha \) is \( a/W \).

3. Results and discussion

3.1. Microstructure and phase analysis

Fig. 2(a)–(c) shows optical microscopy of the laminated composites prepared by P1, P2 and P3 conditions, respectively. Dark layer is Nb and bright layer is Nb-aluminide transformed originally from pure Al sheet by SHS reaction during the process. Nb and the intermetallic compound layers are well laminated alternatively and there is no defect at the interface. However, large and small defects are visible within the intermetallic compound layers in Fig. 2(a) and (b), but only small defects in Fig. 2(c). Two or three distinctive layers are also visible within the intermetallic compound layer in Fig. 2(a) and (b).

Fig. 3 shows X-ray diffraction pattern of the sample prepared by P1 condition, showing the formation of NbAl\(_3\), Nb\(_2\)Al and Nb\(_3\)Al intermetallic compound phases coexisting with pure Nb.

Fig. 4 shows the comparison of X-ray diffraction patterns obtained by P1, P2 and P3 processed samples. Compared with P1, the diffraction of P2 and P3 show high intensities of Nb, NbAl\(_3\) and Nb\(_2\)Al peaks and almost no NbAl\(_3\) diffraction peak. However, P2 shows high intensities of Nb and Nb\(_2\)Al diffraction peaks, whereas P3 shows high intensities of Nb and NbAl\(_3\) diffraction peaks which indicate the possibility of microstructural control of intermetallic compounds by the final holding temperature.

Based on the X-ray results, SEM and EDS spot and line
analysis were carried out to investigate the phase structure constituting the intermetallic compound layer.

Fig. 5(a) shows an SEM image of the laminate structure of the sample prepared by P1 condition. The structure consists of two layers, that is, dark region of Nb layer and bright region of intermetallic compound layer. Darker and brighter regions within the intermetallic compound layer of multi-layer also observed in Figs. 2(a) and 5(b) show compositional variation of Fig. 5(a) by EDS line analysis. The Al concentration profile within the intermetallic compound region changes in three stages, marked X, Y and Z: region X showing low Al concentration with thickness of approximately 10 μm near the interface; region Y showing higher Al concentration than region X with thickness of 20 μm; and region Z showing highest Al concentration with thickness of approximately 10 μm near the center of the intermetallic compound layer.

In order to further examine the Nb and Al concentrations in the intermetallic compound layer, EDS spot analysis was carried out. Fig. 5(c)–(e) shows element spectrums of positions A, B, C, positions D, E, F and positions G, H, I, respectively, marked in Fig. 5(a). The Al spectrum intensity increases towards the center of the intermetallic layer, which is in good agreement with the EDS line analysis, shown in Fig. 5(b). The result of quantitative analysis is shown in Fig. 6. The Al concentrations were 21, 35.5 and 72 at.% for regions X, Y and Z, respectively, which corresponds to Nb2Al, Nb2Al and NbAl3 phases, respectively. This is in good agreement with the X-ray analysis, shown in Figs. 3 and 4.

The formation sequence of the laminate structure within the intermetallic layer is that NbAl3 phase is formed by SHS reaction, followed by formation of new phase layers through diffusion and reactive diffusion [35]. The laminate structure within the intermetallic layer can be concluded to be Nb/Nb2Al/NbAl3 or Nb/Nb2Al/Nb2Al/NbAl3, that agrees well with the phase diagram prediction.

3.2. Mechanical properties

Fig. 6 shows the change in microvickers hardness within the intermetallic compound layer prepared by P1 condition. Microvickers hardness is 190, 980, 790 and 600 Hv for Nb, Nb3Al, Nb2Al and NbAl3 layers, respectively. These microvickers hardness values are nearly the same or slightly higher than other reports on Nb-aluminide based
composites, that reveal 130–170 [36,37], 910 [38], 810 [38] and 460–580 Hv [38,39] for Nb, NbAl, Nb$_3$Al and NbAl$_3$ layers, respectively. This suggests that the thin-foil hot press process is very effective in manufacturing internal defect-free and fine structured intermetallic compound phases. Another interesting result is that hardness within the intermetallic compound layer decreases with increasing Al/Nb atomic ratio per unit cell, which is similar with Fe–Al system intermetallic compound where hardness also decreases with increasing Al/Fe atomic ratio. However, in Ti–Al system intermetallic compound, hardness increases with increasing Al/(Ti, Ni) atomic ratio [11].

Generally, mechanical properties of most intermetallic compounds are related to Peierls stress, which is the resistance to slip in crystal. Peierls stress depends on several factors, e.g. intermetallic compound crystal structure, crystal symmetry, complexity of the crystal structure, unit cell size, bonding between elements and microstructure [40–42]. Fig. 7 shows the stress–strain curves of P1 and P3 samples obtained by tensile test. P1 sample shows the ultimate tensile strength (UTS) and elongation of 86 MPa and 6.6%, respectively, whereas P2 sample shows 115 MPa and 14.5%, respectively. The yield strength and UTS values of both P1 and P3 samples are considerably lower than 335 MPa, reported by Rowe et al. [43]. Also, these values are lower than pure Nb which has yield strength and UTS values of 123–204 and 195–277 MPa, respectively. The samples prepared in this work have an intermetallic compound layer thickness in several hundredth μm, whereas sample prepared by Rowe et al., has intermetallic compound layer thickness in several tenth μm. Intermetallic compounds have high compressive strength but low tensile strength, and intermetallic compound layer fractures prior to the metal layer during tensile test and the remained metal layer has to sustain the load, that causes the decrease of tensile strength. The thickness and volume fraction of metal layer affect tensile properties of the laminate composites. Another reason for lower values of yield strength and UTS in P1 and P3 samples than pure Nb is also considered to be microstructural coarsening of the Nb layer during high-temperature synthesis. The elongation of P3 sample is almost twice as large as that of the P1 sample. Comparing the stress–strain curves of P1 and P3 samples, P1 shows nearly no strain hardening, but P3 shows considerable strain hardening. This is attributed to the thicknesses of the ductile Nb layer and the brittle intermetallic compound layer. Since thickness of Nb layer in P1 sample is thinner than that of P3 sample, less plastic deformation occurs in P1 sample. Also, various defects within the intermetallic compound layer in P1 sample may affect the fracture in intermetallic phase.

Fig. 8(a) and (b) shows P1 sample sectioned near the fractured surface after tensile test in longitudinal and transverse directions, respectively. Fig. 8(c) and (d) shows P3 sample sectioned near the fractured surface after tensile test in longitudinal and transverse directions, respectively. For each transversely sectioned sample, microcracks (arrowed A) are observed mainly in the intermetallic compound layer normal to the load direction, and Nb layer shows deformation along the load direction. Sharp microcracks in the intermetallic compound layer of P1 sample, arrowed A in Fig. 8(a), are observed and no coalescence between microcracks are found near the fractured surface. However, microcracks of P3 sample, arrowed A and B in Fig. 8(c), are opened in parallel to the load direction not only near the fracture surface, but also away from the fracture surface. Especially, microcracks coalesced in the loading direction near the fractured surface and formed voids. However, there is no crack at the interface between the intermetallic compound and the metal layers in both samples.

At the fracture surface of sample, brittle fracture is observed in the intermetallic compound layer. However, the Nb layer is deformed in the load direction and ductile chisel edge fracture is observed at the center of the fractured surface. P3 sample demonstrates sharper chisel edge than P1 sample. Chisel edge fracture in laminate composites seems
to be related to the thickness of the metal and the intermetallic compound layers, the fracture mode of the intermetallic compound layer and the coalescence of microcracks near the fractured surface. Thus, microcrack size is proportional to the intermetallic compound layer thickness, and the metal layer acts as a ductile reinforcement. Void formation was not observed due to coalescence of microcracks near the fractured surface in P1 sample. Since the intermetallic compound layer is strongly bonded to the metal layer, the metal layer can deform after the intermetallic compound layer fractures during the tensile test. As metal layer thickness in P3 sample is relatively thinner than that of P1 sample, P3 sample demonstrated the development of chisel edge fracture compared with P1 sample and considerably large voids in P3 sample are observed in the fractured surface near the intermetallic compound layer. This behavior causes that P3 sample has higher elongation and toughness compared with P1 sample.

Fig. 9 shows the fracture toughness of P1 and P3 samples, calculated from the maximum loading point in the COD (crack opening displacement) curves during 3-point notch bending test. Fracture toughness of P1 sample with loading in the crack arrester direction is 9.7 MPa m$^{1/2}$. Fracture toughness of P3 sample with loading in crack divider and arrester directions is 11.2 and 12.4 MPa m$^{1/2}$, respectively. The fracture toughness of P1 sample in the crack arrester direction is higher than P3 sample. And P3 sample has higher fracture toughness value in crack arrester direction than crack divider direction. Fracture toughness values are in good agreement with that reported by Heathcote et al. [37].

4. Conclusions

Thin foil hot press process with proper combination of synthesis reaction temperature and time can be used to manufacture metal/intermetallic compound laminate composite. It is possible to control microstructure, phase and thickness in the intermetallic compound layer by changing the synthesis reaction cycle.

In the present work, Nb/Nb-aluminate system laminated composites were manufactured from pure Nb and Al sheets, consisting of fine Nb/Nb$_2$Al/NbAl$_3$ or Nb/Nb$_2$Al/Nb$_2$Al/NbAl$_3$ structure in the intermetallic compound layer. During the process, the NbAl$_3$ phase is initially formed by SHS reaction, and nucleation and growth of the Nb$_2$Al phase near the Nb layer interface is followed by diffusion of Al from the NbAl$_3$ phase. Then Nb$_2$Al phase formed near the interface provides Al to diffuse into the Nb layer and to form Nb$_2$Al, which is the most stable phase in Nb-rich region in the phase diagram. Microuckers hardness in the intermetallic compound layer shows variation due to the formation of various phases, and the microcrickers hardness value decreases with increasing Al/Nb atomic ratio.

Since the intermetallic compound layer fractures prior to the metal layer, tensile strength of the laminate composite is affected by the thickness and volume fraction of metal layer. Chisel edge fracture was observed in the fracture surface after tensile test that are related to the thickness of the metal and the intermetallic compound layers. The laminate composites demonstrate high ductility of 6.6–14.5% and fracture toughness of 9.7–12.4 MPa m$^{1/2}$ due to strong bonding at the interface between the metal and the intermetallic compound layers interface.

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