Synthesis of Porous Al₃Ti/Al Composite and Effect of Precursor Processing Condition on Cell Morphology

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Porous Al₃Ti/Al composite was fabricated by a combustion foaming process, which makes use of exothermic reactions between titanium, aluminum and boron carbide powders. Boron carbide powder was used as an exothermic agent to increase the heat of reaction. Fundamental combustion foaming behavior and effects of processing parameters (Al/Ti blending ratio, addition of exothermic agent and powder compacting pressure) on the foaming behavior were investigated. Combustion foaming took place over temperature ranges between melting points of aluminum and Al₃Ti. Exothermic agent addition turned out to be effective to increase the porosity of porous Al₃Ti/Al composite. Relative density of the precursor was an important factor, which needed to be higher than a threshold level (0.67) to prevent extremely inhomogeneous pore morphology. By conducting hot extrusion to the precursor, both pore size and porosity were increased. As a result of compressive test, high plateau stress and absorbed energy were achieved by increasing Al/Ti mole blending ratio from 4.0 to 7.0.

[doi:10.2320/matertrans.L-M2009823]

(Received May 18, 2009; Accepted July 31, 2009; Published October 25, 2009)

Keywords: porous material, foam material, intermetallics, composite, combustion synthesis, compressive test, energy absorption

1. Introduction

Porous materials, which contain large amount of pores or voids inside, have been investigated as potential candidates for crash elements, thermal barriers, damping materials due to their unique mechanical and physical properties.¹⁻³⁾ Porosity and cell morphology are important factors to control the properties (strength, modulus, thermal conductivity, and so forth).⁴⁾ Among many kinds of porous metals, porous aluminum is most enthusiastically investigated.⁵⁻¹⁰⁾ To say nothing of the low density of aluminum itself, one reason is that effective blowing agents like TiH₂, ZrH₂ and CaCO₃, which decompose and release gaseous phase at around the melting point of aluminum or aluminum alloys,¹¹⁻¹⁵⁾ are available. Another reason is that the melting point of aluminum is relatively low (933 K) and the processing temperature is easily achieved by a conventional electric furnace. If metals can be substituted by intermetallics or their composites, such porous materials can be used under extremely severe environments, e.g. thermal barrier coatings at high temperatures and heavy load-bearing components.¹⁶⁻¹⁸⁾ However, the melting point of intermetallics is generally higher than that of light metals, and it is more difficult and more energy consuming process to introduce pores inside intermetallics. Combustion synthesis is one of the attractive processing routes for producing intermetallics and their composites because high melting point material can be produced with little energies and without special equipments.^{19,20)} The authors have developed a fabrication process for porous intermetallics using combustion synthesis, and reported porous nickel aluminide with porosities more than 80%.²¹⁻²⁴⁾ In this study, we investigated the combustion foaming process of porous Al₃Ti/Al composite. Figure 1 shows a brief outline of the combustion foaming process for the synthesis of porous Al₃Ti/Al composite. Fundamentally,

Fig. 1 Schematic illustration of combustion foaming process to synthesize porous Al₃Ti/Al composite.

a reaction between aluminum and titanium, which synthesizes Al₃Ti, was utilized.

As shown in Fig. 1, boron carbide (B₄C) powder was also blended in the powder compacted precursor. B₄C powder reacts with titanium, and generates large amount of reaction heat as shown in the next equation.

This heat of reaction assists the progress of the Al₃Ti formation and is expected to enhance the foaming behavior. Therefore, B₄C and equivalent amount of titanium, which is required for eq. (2), was used as “exothermic agent” in this study. In the present paper, we report the fundamental combustion foaming behavior of porous Al₃Ti/Al composite, and discuss the effect of exothermic agent powder addition and powder compacting pressure on pore morphology. Compressive mechanical property is also reported.

2. Experimental Procedure

2.1 Fabrication of porous Al₃Ti/Al composite

Aluminum (<45 μm, 99.99%), titanium (<45 μm, 99.9%)

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Table 1 Volume fraction of Al, Al₃Ti and ceramic particles (TiB₂ and TiC) in the solid section of each specimen.

Al/Ti mole ratio	4.0		7.0	
Exothermic powder addition	0	10	0	10
Volume fraction of Al	21	19	49	44
Volume fraction of Al ₃ Ti	79	71	51	46
Volume fraction of TiB ₂ ,TiC	0	10	0	10

Unit: vol%

Fig. 2 Schematic illustration of induction heating apparatus.

Fig. 3 Sequential photos of precursor during combustion foaming process (Al/Ti mole ratio: 4.0, exothermic agent addition: 10 vol%).

and B₄C (ave. 10 μ m, 99%) powders were used as starting elemental powders. First of all, aluminum and titanium powders were blended (Al/Ti mole blending ratio: 4.0 or 7.0). As the exothermic agent, B₄C powder and equivalent amount of titanium, which was spent for the reaction shown in eq. (2), were additionally blended in the starting powder. The amount of exothermic agent was fixed to produce 10 vol% ceramic particles (TiC, TiB₂) in the solid section of porous specimen. Calculated volume fraction of Al, Al₃Ti and ceramic particles are listed in Table 1. The calculation was carried out assuming that the reactions shown in eq. (1) and eq. (2) proceeded completely (i.e. titanium and B₄C are completely transformed to Al₃Ti, TiB₂ and TiC). After titanium, aluminum and B₄C were blended, the blended powder was compacted either by single-axis pressing at room temperature (30, 50, 100 and 165 MPa) or by hot extrusion at 400°C (240 MPa, extrusion ratio: 7.1) to make cylindrical shape precursors (ϕ = 15 mm, h = 15 mm). Prior to the hot extrusion, blended powder was cold compacted by 400 MPa. The compacted powder preform was directly hot extruded in air (i.e. the preform was not canned). The precursor was inserted into a quartz tube filled with argon gas, and then heated by high-frequency induction (420 kHz) to induce the combustion reaction (Fig. 2). The apparent density of the porous specimen was measured by Archimedes method to

calculate the porosity. Area of each individual pore was measured by image analyzing software to calculate diameter of equivalent area circle. Pores smaller than 0.196 mm² (equivalent to 0.5 mm in diameter) were neglected to guarantee the accuracy of analysis. In all specimens, total volume fraction of the neglected pores was less than 1% among all pores.

2.2 Evaluation of mechanical property

Compressive test of the porous specimen (Al/Ti: 4.0, exothermic agent addition: 10%) was carried out with initial strain rate of $2.7 \times 10^{-3} \text{ s}^{-1}$. Cylindrical sample (ϕ 25 mm $\times$ h25 mm) was prepared for the test. Plateau stress and energy absorption were calculated by average stress between 20 and 30% strain and area under the stress-strain curve up to 50% strain as indicated in JIS H 7902 (Method for compressive test of porous metals).

3. Results and Discussion

3.1 Fundamental behavior of combustion foaming

Figure 3 shows the sequential photos of precursor during the combustion foaming process (Al/Ti mole ratio: 4.0, exothermic agent addition: 10 vol%). Figure 4 shows temperature-time relation of the specimen during the combustion

Fig. 4 Time-temperature chart of precursor during combustion foaming process. Symbols (a) through (e) correspond with the photos shown in Fig. 3.

Fig. 5 Cross section of porous specimen (Al/Ti mole ratio: 4.0, exothermic agent addition: 10 vol%).

foaming process measured by a thermocouple directly embedded in the center of the precursor. Symbols from (a) to (e) in Fig. 4 correspond to the photos shown in Fig. 3. The original cylindrical shape of the precursor was maintained until the onset of the combustion reaction (Fig. 3(a)). The exothermic behavior of the precursor is clearly understood by the emission of visible light (Figs. 3(b) and (c)). This reaction started at around the melting point of aluminum, with a sharp increase in the temperature as shown in Fig. 4. The reaction took about 10 s and the maximum temperature reached to the melting point of Al₃Ti (1613 K). The apparent expansion of the precursor from cylindrical shape to spherical shape (photos (a) and (d) in Fig. 3) indicates that the pore formation took place during this combustion period. We already reported that the pores in porous Al₃Ni intermetallics were formed mainly by dissolved hydrogen and adsorbed water which originally existed in the starting powders, and major gas component in pore was hydrogen.²⁴⁾ The same foaming mechanism is considered to take place in this specimen as well. The cross section of the porous specimen (Al/Ti mole ratio: 4.0, exothermic agent addition: 10 vol%) is shown in Fig. 5. The porosity of this specimen was 74%, which was much higher than that of the precursor before heating (17%). The pore size was smaller at the periphery of the specimen than at the center. This is caused by the intrinsic nature of the combustion process, in which combustion temperature of the specimen at the center is higher than the peripheral part.

However, this inhomogeneity was relaxed by increasing compacting pressure of precursor as described in the following section.

3.2 Effect of exothermic agent addition

Figures 6 and 7 show cross section and equivalent pore diameter histogram of porous specimens with and without exothermic powder addition (Al/Ti mole ratio: 4.0 and 7.0). The number on upper right of each photo in Fig. 6 indicates porosity of porous specimen. Average pore sizes are shown in Fig. 7. Porosity of the specimens with exothermic agent addition was higher than 70%, whereas that of specimens without exothermic agent was below 50%. It is obvious that the porosity was effectively increased and pore size became larger by adding exothermic agents. The authors have already reported that addition of B₄C powder assisted the foaming behavior of porous Al-Ni intermetallics because heat of reaction between B₄C and titanium is higher than that of Al₃Ni formation.^{21–24)} In this experiment, the heat of reaction shown in eq. (2) is also much higher than that of eq. (1). Therefore, the exothermic agent was quite effective to assist the combustion foaming behavior of porous Al₃Ti/Al composite.

3.3 Effect of compacting method of precursor preparation

Figure 8 shows cross section of porous specimens (Al/Ti mol ratio: 4.0, exothermic agent: 10 vol%), showing the effect of compacting pressure on pore morphology of porous specimens. Precursors were prepared either by single-axis compaction at room temperature (30–165 MPa) or by hot extrusion at 400°C (240 MPa). Table 2 shows average pore size and porosity of porous specimens together with relative density and porosity of precursors. The relative density of precursor became higher by increasing the compacting pressure. The highest porosity of porous specimen (85%) was achieved when precursor was fabricated by hot extrusion. One reason for the high porosity of the hot-extruded precursor may be that high relative density of precursor prevented the dissipation of gas phase to the ambient atmosphere. Inhomogeneous distribution of pore size, caused by the intrinsic nature of combustion reaction as shown in Fig. 5, was observed in the porous specimens when the precursors were fabricated by cold compaction, whereas such inhomogeneity was not observed when the precursor was made by hot extrusion. Higher thermal conductivity of high-density precursor may result in the homogeneous temperature distribution during the combustion process. As a consequence, homogeneous distribution of pore size was achieved.

3.4 Compressive deformation behavior

Porous materials show high energy absorption capacity,²⁵⁾ because large compressive deformation at nominally constant stress so-called “plateau stress region”²⁶⁾ is emerged in compressive stress-strain relationship. This is one of the most unique properties of porous materials, which makes them applicable to crash elements.^{27,28)} The stress-strain curves of two samples (Al/Ti mole ratio: 4.0 and 7.0, exothermic agent: 10 vol%, precursor preparation method: single-axis compaction at 165 MPa) are shown in Fig. 9. As a compa-

Fig. 6 Cross section of porous specimens synthesized from precursors with and without exothermic agent addition (Al/Ti mole ratio: 4.0 and 7.0). The number on upper right of each photo indicates porosity of porous specimen.

Fig. 7 Histogram of pore diameter of porous specimens. (a) Al/Ti mole ratio: 4.0, exothermic agent: nil, (b) Al/Ti mole ratio: 7.0, exothermic agent: nil, (c) Al/Ti mole ratio: 4.0, exothermic agent: 10 vol%, (d) Al/Ti mole ratio: 7.0, exothermic agent: 10 vol%.

rative material, the data of porous 6061 aluminum fabricated from TiH_2 /6061Al precursor (powder processing route) is also shown. The density of porous material, plateau stress, absorbed energy per unit volume and energy absorption

efficiency of each specimen are listed in Table 3. The plateau stress of the specimen (Al/Ti: 4.0) was at the same level of porous 6061 aluminum, even though the density was approximately the half. Moreover, the plateau stress of the

Fig. 8 Cross section of porous specimens synthesized from precursors compacted at various pressures (Al/Ti mole ratio: 4.0, exothermic agent addition: 10 vol%).

Table 2 Average pore size and porosity of porous specimens and relative density (porosity) of precursors fabricated with various compacting pressures.

Compacting pressure	30 MPa	50 MPa	100 MPa	165 MPa	240 MPa (Hot extrusion)
Average pore size of porous material	2.9 mm	2.6 mm	2.8 mm	2.5 mm	4.3 mm
Porosity of porous material	73%	75%	77%	74%	85%
Relative density (porosity) of precursor	0.63 (37%)	0.67 (33%)	0.76 (24%)	0.83 (17%)	0.95 (5%)

Fig. 9 Compressive stress-strain curves of porous Al₃Ti/Al composite and porous 6061Al.

specimen (Al/Ti: 7.0) was 4 times higher than the one with low Al/Ti ratio specimen (Al/Ti: 4.0). This implies the potentiality of Al₃Ti/Al porous composite as a heavy load-bearing crash element in comparison with the conventional aluminum foam. Wang *et al.* reported the strength of Al₆₇Ti₂₅Cr₈/Al composites (volume fraction of aluminum: 10%) made by reactive process was higher than monolithic Al₆₇Ti₂₅Cr₈.²⁹⁾ They reported two strengthening mechanisms

of aluminum addition; (i) sufficient amount of molten aluminum buried micro-pores and micro-cracks in intermetallics and (ii) ductile aluminum, which encircled brittle Al₃Ti phase, caused the effective transfer of load from the soft aluminum to the reinforcing Al₃Ti phase. The same mechanism might be working in this experiment as well.

4. Conclusions

Porous Al₃Ti/Al composite was fabricated by a combustion reaction between aluminum, titanium and B₄C powders. Fundamental combustion foaming behavior and effects of the precursor preparation conditions on the porosity and pore morphology of the synthesized porous materials were investigated. The following results were obtained in this experiment.

(1) Foaming behavior of powder compacted precursor was observed during the combustion period which took place over temperature ranges between melting point of aluminum and Al₃Ti.

(2) Porosity of porous Al₃Ti/Al composite was effectively increased by adding exothermic agent powder (B₄C and titanium blended powder).

(3) Pore size of the porous specimen made from cold compacted precursor was smaller at the periphery than at the center.

Table 3 Plateau stress, absorbed energy and energy absorption efficiency of porous Al₃Ti/Al composite and porous 6061Al.

	Density (g·cm ⁻³)	20–30% average plateau stress (MPa)	Absorbed energy per unit volume (MJ·m ⁻³)	Energy absorption efficiency (%)
Al/Ti = 4.0	0.25	13	7.1	65
Al/Ti = 7.0	0.29	52	27	86
6061Al	0.49	14	6.8	90

(4) Pore morphology of the porous specimen tended to be extremely inhomogeneous when compacting pressure of precursor was not high enough. Both porosity and pore size were increased by applying hot extrusion to the precursor.

(5) The plateau stress of the porous specimen (Al/Ti: 4.0) was at the same level of porous 6061 aluminum, even though the density was approximately the half. The plateau stress of the specimen (Al/Ti: 7.0) was 4 times higher than the one with low Al/Ti ratio specimen (Al/Ti: 4.0).

Acknowledgement

This study was supported by Industrial Technology Research Grant Program in 2008 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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