

Reactive processing of ultra-light iron foam with high specific stiffness

超軽量・高比剛性を有する鉄系フォーム材料の反応合成

Makoto Kobashi, Department of Materials Science Engineering, Nagoya University

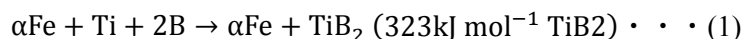
名古屋大学 小橋 眞

1 introduction

Porous metals have unique properties such as high-specific stiffness, damping capacity, heat insulating effect and so forth. By these characteristics, they are expected to be applied to impact absorbers, sound absorption panels and compact heat exchangers [1]. Porous aluminum alloys have been studied by many researchers [2-4], and nowadays iron based porous metals are also researched since they possess several attractive properties such as high strength, high stiffness, high melting temperature and compatibility with steel components [5-9]. However, there are some difficulties to manufacture iron based porous materials. For example, high temperature near the melting point of iron is required for the fabrication, and the drainage occurs easily because the specific gravity of iron is larger than that of aluminum.

The applicants have developed an innovative manufacturing process, “reactive precursor method”, in which the precursors consisting of at least two elemental powders are used. The elemental powders should react with each other and release high heat of formation to let the combustion reaction happen [10-15]. Once the combustion reaction occurs, inorganic compounds (ceramics or intermetallics) are synthesized and the temperature of the reaction products increases rapidly due to the heat of formation. It is known that the specimens after the combustion reaction are usually porous. The residual atmospheric gas originally existed in the precursor and the released gases originally adsorbed at or absorbed in the elemental powders are the main sources of the pores. Since the combustion reaction generates large amount of heat, the specimen’s temperature is much higher than the atmospheric temperature during the reaction. Therefore the cooling rate is very fast and the solidification occurs rapidly. This is also an advantage to avoid the severe drainage.

In this research, we chose three elemental powders (iron, titanium and boron) as starting powders. By heating the blended [Fe+Ti+B] powder, a combustion reaction shown below occurs.



By changing the α in eq.(1), the volume fraction of TiB_2 in iron can be controlled. It is reported that the TiB_2 is thermodynamically stable in iron and suitable as the strengthening ceramics in iron. Aside from releasing the large amount of heat of reaction, TiB_2 particles play another important role to increase the viscosity of molten iron, which can stabilize the foam structure. Additionally, the interface bonding between iron and TiB_2 is reported to be strong and the dispersion of TiB_2 particles improves the stiffness of iron.

The objective of this research is to develop a processing technique to manufacture porous Fe/ TiB_2

composites from the reactive precursors. In this research, the carbon powder was added in order to control the pore morphology and porosity (foaming agent). We investigated the effect of the volume ratio of TiB₂ addition on the foaming behavior and also the effect of various foaming agent on porosity.

2 Experimental Procedures

Iron powder (3-5 μ m, 99.99%), titanium powder (<45 μ m, 99.9%) and boron powder (<45 μ m, 99%) were blended to synthesize 20 to 70vol% TiB₂ particles in Fe/TiB₂ composites after the reaction (1). A foaming agent powder was added to the blended powder. The additive amount of carbon was varied from 1.0 to 5.0mass%. The blended powder was compressed into a cylindrical shape (ϕ 10 \times h10 mm) by a uniaxial cold-pressing under 200MPa. The relative density of the precursors was about 0.67. The precursor was heated in an induction furnace under an argon atmosphere to induce the combustion reaction (heating rate: 3.5 $^{\circ}$ C \cdot min⁻¹). The specimen was cooled in the furnace immediately after the glow of the combustion reaction was observed. The porosity of the specimen was measured by an Archimedes method. The cross section of the specimen was observed by a scanning electron microscope (SEM). The temperature profile during the combustion reaction was measured by inserting a thermocouple in the specimen. The quantitative analysis of a gas phase in the pore was carried out by an inert gas fusion infrared absorption method (LECO TS 600). The carbon concentration in the iron powder was measured by a combustion-infrared absorptiometric method (LECO CS444).

3 Results and Discussion

3.1 Reaction between Fe, Ti and B powder

Fig.1 shows adiabatic temperatures of the combustion synthesized specimens with various volume fractions of TiB₂. The adiabatic temperature is the calculated maximum attainable temperature of the specimen during the combustion reaction on the assumption that the specimen is under the adiabatic state. In this experiment, the adiabatic temperature was calculated by the following equation.

$$\Delta H_f + \int_{T_0}^{T_m} C_{p,Fe} dT + \Delta H_{melt,Fe} + \int_{T_m}^{T_{ad}} C_{p,Fe} dT + \int_{T_0}^{T_{ad}} C_{p,TiB_2} dT = 0 \quad (2)$$

Where ΔH_f is the heat of formation (J), ΔH_{melt} is the heat of fusion (J), T_0 is the initial temperature (K), C_p is the heat capacity ($J \cdot mol^{-1} \cdot K^{-1}$), T_m is the melting temperature of iron and T_{ad} is the adiabatic temperature of combustion (K).

In order to fabricate closed-cell-type porous metals by combustion reactions, the adiabatic temperature must exceed the melting point of the metal.

The maximum temperature did not exceed the melting point of iron, when TiB₂ volume fraction was blow 20 vol%. When TiB₂ volume fraction reached to 70vol%, the maximum temperature exceeded the boiling point of iron. This extremely high adiabatic temperature often ended up with the explosion

of the specimen during the combustion reaction. According to this calculation, we decided to carry out this experiment with TiB₂ volume fractions in between 20 and 70vol%.

Fig.2 shows the cross sections of the specimens with 20~70vol% TiB₂. With 20vol% TiB₂ dispersion, the glow of the combustion reaction was very weak and the closed pores were not observed. With 30~60vol% TiB₂ dispersion, the glow of the combustion reaction was clearly observed and closed pores were formed (pore sizes are about 1mm). With 70vol% TiB₂ addition, the specimen exploded. The explosion occurred because the adiabatic temperature exceeded the boiling point of iron.

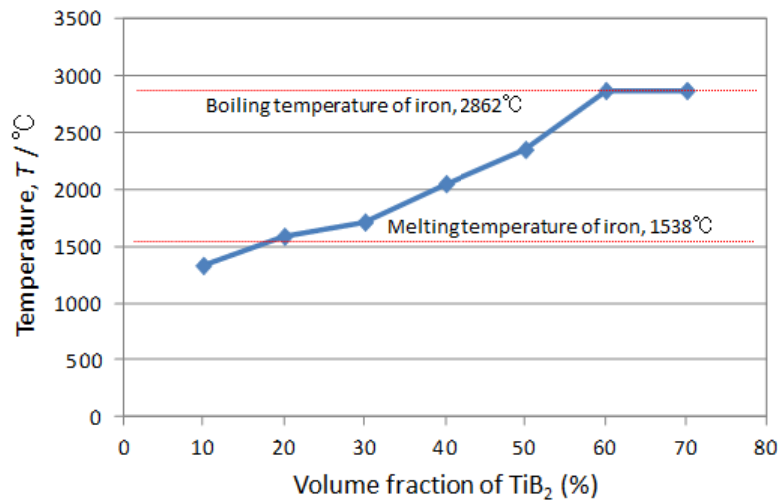


Fig.1 Adiabatic temperature of the specimens with various TiB₂ volume fractions.

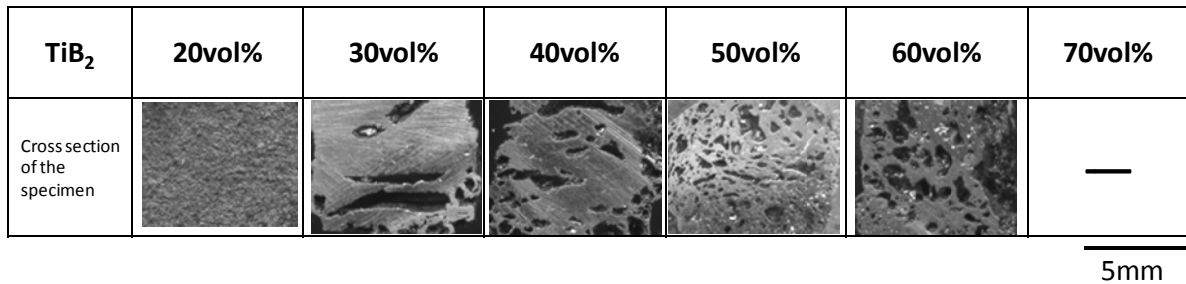


Fig.2 Cross sections of the specimens with various volume fractions of TiB₂.

Fig.3 shows the microstructure of the cell wall (50vol%TiB₂). TiB₂ particles (2-3μm) were uniformly dispersed in the iron matrix. Fig.4 shows the temperature profile during the combustion reaction. Ignition temperature was confirmed as 960°C. This temperature is about much lower than the melting point of iron. Ignition temperatures were nearly constant (about 950°C) regardless of the volume fraction of TiB₂. Although the maximum temperature could not be measured correctly, it is apparent that the combustion reaction occurred in a short time. The temperature of the specimen exceeded the melting point of iron for about only 2 seconds. Based on these results, We mainly

researched the effect of foaming agents for the specimens with 30~60vol%TiB₂ in the following sections.

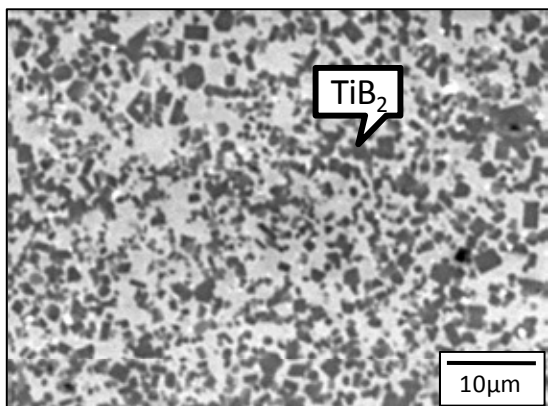


Fig.3 SEM micrograph of the specimen of 50vol%TiB₂ without foaming agent.

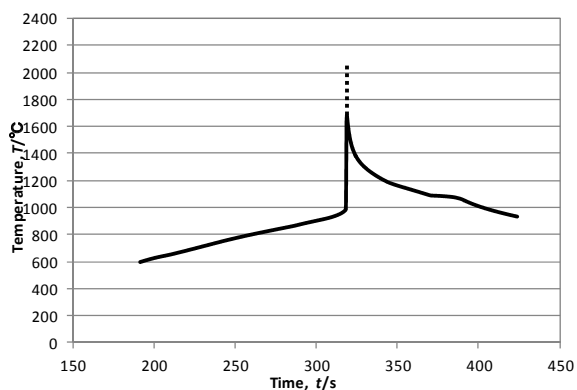


Fig.4 Temperature profile of the specimen of 50vol%TiB₂ without foaming agent.

3.2 Effect of carbon additive amount

In this section, the effect of the carbon additive amount is discussed. Fig.5 shows cross sections of the specimens with 0~5.0mass%C additions (TiB₂ volume fractions: 30~60vol%). When carbon additive amounts were 1.0 and 2.0mass%, both the number of pores and the pore size were increased in comparison with the non-added specimen. The porosity of the specimen prepared with 50vol%TiB₂ and 3.0mass%C showed the highest value (60%). The closed pores were no longer formed by adding 3.0 and 4.0 mass%C when TiB₂ volume fractions were 30, 40% and 50%.

Fig. 6 shows the porosities of the specimens with 1.0~3.0mass%C additions. Porosities of the specimens with 1.0, 2.0 and 3.0mass%C additions were 48%, 51% and 60%, respectively. Fig. 7 shows the macroscopic and microscopic cross-sections of the specimen with the 3.0mass%C addition. The pore size was about 800μm and the closed cell-structure was apparent (Fig. 7(a)). TiB₂ particles (2-3μm) were uniformly dispersed in the iron matrix (Fig. 7 (b)). Fig. 8 shows the microstructure of the specimen with 5.0mass%C addition. The cell structure of the specimen changed to an open-cell type with the pore size under 100μm. Fig. 9 shows calculated adiabatic temperatures of the combustion synthesized specimen with various carbon additive amounts. Fig. 10 shows temperature profiles of the specimens with 0, 3.0 and 5.0mass%C additions. According to Fig. 9, it is apparent that the theoretical adiabatic temperature is not significantly affected by the carbon additive amount. Nevertheless, with respect to the practical temperature profiles, the maximum temperatures exceed the melting point of iron when carbon additive amounts are 0 and 3.0mass%, but the exothermic peak of the specimen with 5.0mass%C addition was lower than the melting point of iron. In this case, the presence of the carbon powder between titanium and boron powders, and might prevent the reaction.

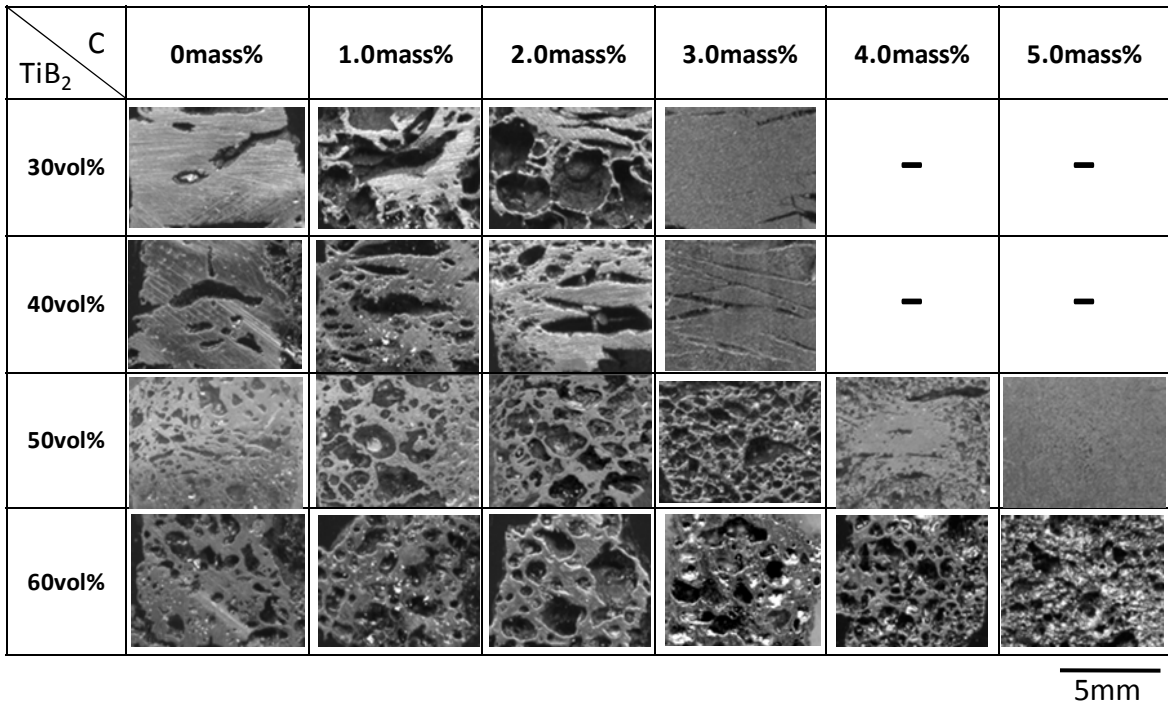


Fig.5 Cross sections of the specimens with 0~5.0mass%C additions (30~60vol%TiB₂)

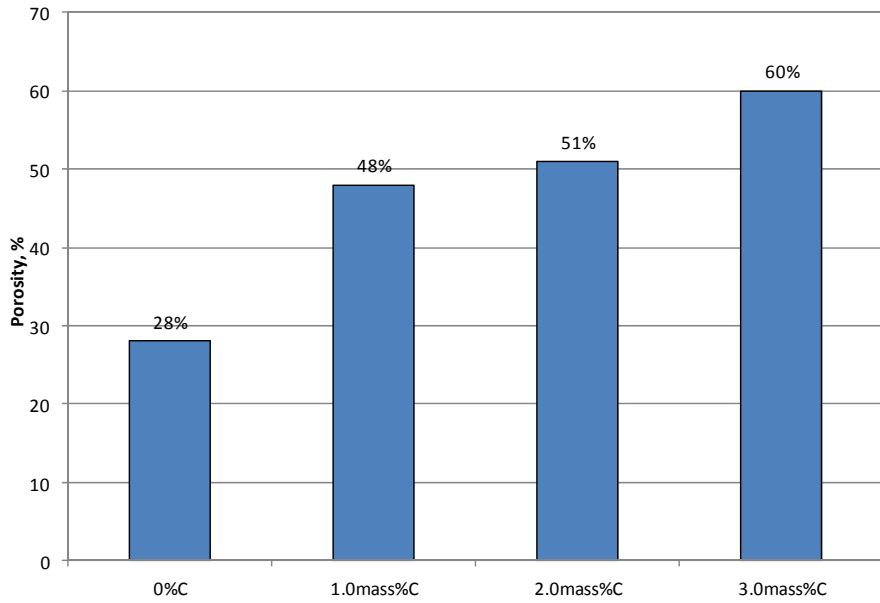


Fig. 6 Porosities of the specimens with 0~3.0mass%C additions (TiB₂ 50vol%).

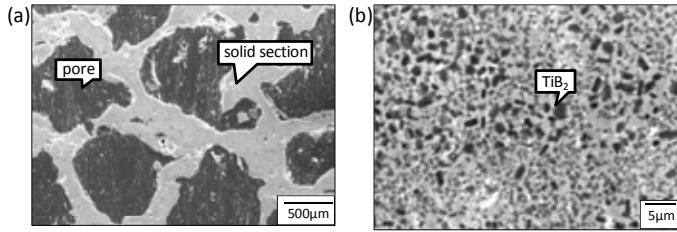


Fig. 7 SEM micrographs of the specimen with a 3.0mass%C addition (50vol%TiB₂) (a)Macroscopic cross-section, (b) microstructure

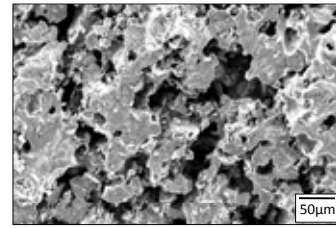


Fig. 8 SEM micrograph of the specimen with 5.0mass%C addition (50vol%TiB₂)

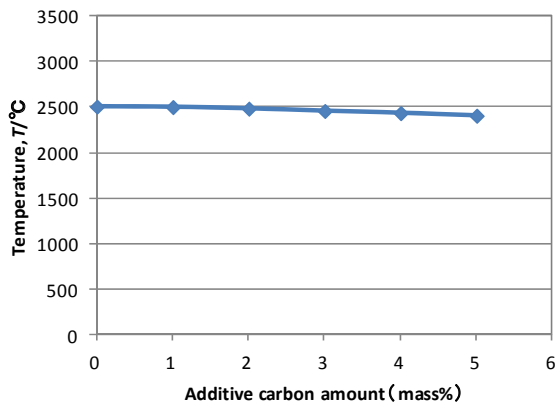


Fig. 9 Adiabatic temperature of the combustion synthesized specimens with various carbon additive amounts (50vol%TiB₂)

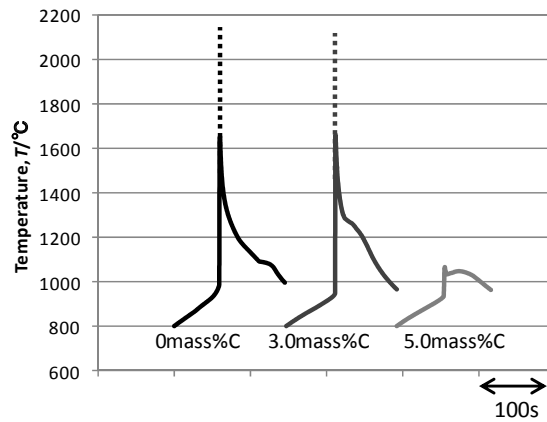


Fig.10 Temperature profiles of the specimens with various amounts of carbon (50vol%TiB₂).

4 Conclusions

To fabricate porous Fe/TiB₂ composites by chemical reaction, the reactive precursor method using iron, titanium, boron powders was investigated. The following results were obtained through the experiment.

- 1) For making porous Fe/TiB₂ composites, the carbon powder turned out to be a suitable foaming agent. The reason why the porosity increases are (i) the melting point of Fe decreases by carburizing and (ii) carbon is oxidized during the combustion process and forms gaseous CO. The oxygen was originally dissolved in the elemental powders.
- 2) When TiB₂ volume fraction was 50% and carbon additive amount was 3.0mass%, the porosity reached the maximum (60%) and the pore size was about 800µm. In the solid section, TiB₂ particles

(2-3 μm) were uniformly dispersed in iron matrix.

3) By increasing carbon additive amount (>4~5mass%), the closed-cell porous material could no longer be obtained. The accessibly added carbon prevented a contact between iron, titanium and boron powders and disturb the reaction.

Acknowledgement

This work was supported by JFE 21st Century Foundation.

References

- [1] J. Banhart, Manufacture, characterization and application of cellular metals and metal foams. *Prog Mater Sci*, **46** (2001), pp. 559–632.
- [2] Y. Chino, H. Nakanishi, M. Kobata, H. Iwasaki and M. Mabuchi, Processing of a porous 7075 Al alloy by bubble expansion in a semi-solid state. *Scr Mater*, **47** (2002), pp. 769–773.
- I. Duarte and J. Banhart, A study of aluminium foam formation-kinetics and microstructure. *Acta Mater*, **48** (2000), pp. 2349–2362.
- [3] B. Matijasevic and J. Banhart, Improvement of aluminium foam technology by tailoring of blowing agent. *Scr Mater*, **54** (2006), pp. 503–508.
- [4] B.H. Smith, S. Szyniszewski, J.F. Hajjar, B.W. Schafer, S.R. Arwade, Steel foams for structures: A review of applications, manufacturing and material properties, *Journal of constructional Steel Research*,(2011)
- [5] C. Park and S.R. Nutt, PM synthesis and properties of steel foam. *Mater Sci Eng A*, **A288** (2000), pp. 111–118.
- [6] C. Park and S.R. Nutt, Anisotropy and strain localization in steel foam. *Mater Sci Eng A*, **A299** (2001), pp. 68–74.
- [7] C. Park and S.R. Nutt, Strain rate sensitivity and defects in steel foam. *Mater Sci Eng A*, **A323** (2002), pp. 358–366.
- [8] Günter Stephani, Olaf Andersen, Hartmunt Göhler, Cris Kostmann, Kerstin Kümmel, Peter Quadbeck, Matthias Reinfried, Thomas Studnizky and Ulf Waag, *Porous Metal and Metal Foaming Technology* (2005) p.21
- [9] N. Inoguchi, M. Kobashi and N. Kanetake, Combustion foaming process of porous Al₃Ti/Al composite synthesized from elemental powders. *Mat Trans*, **50** (2009), pp. 2609–2614.
- [10] R. Wang, M. Kobashi and N. Kanetake, Effect of powder blending ratio on pore morphology of combustion Processed Al-Ni foams. *Adv Mater Res*, **16-18** (2005), pp. 53–56.
- [11] M. Kobashi, R. Wang, Y. Inagaki and N. Kanetake, Effects of processing Parameters on pore

- morphology of combustion synthesized Al-Ni foams. *Mater Trans*, **47** (2006), pp. 2172–2177.
- [12] N. Kanetake and M. Kobashi, Innovative processing of porous and cellular materials by chemical reaction. *Scr Mater*, **54** (2006), pp. 521–525.
- [13] M. Kobashi, N. Inoguchi and N. Kanetake, Powder size effect on cell morphology of combustion synthesized porous Al₃Ti/Al composite. *Intermetallics*, **18** (2010), 1102-1105
- [14] M. Kobashi and N. Kanetake, Processing of intermetallics foam by combustion reaction. *Adv Eng Mater*, **4** (2002), pp. 745–747.
- [15] A.R. Kennedy and V.H. Lopez, The decomposition behavior of as-received and oxidized TiH₂ foaming-agent powder. *Mater Sci Eng*, **A357** (2003), pp. 258–263.