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Microgravitational Combustion Synthesis

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Abstract: Combustion synthesis technology can be advantageously applied to high-temperature experiments under microgravity environments with the aid of its self-propagating high-temperature reaction process. Combustion synthesis consists of the processes of reaction propagation and product crystallization. Since the former proceeds rapidly, a short-time microgravity environment, even for about 10 s, should be long enough to attain the synthesizing process. In the present work, combustion synthesis of boride, oxide and carbide composites is investigated under microgravity environments formed in a dropping capsule and a plane parabolic flight in order to assess the potential of combustion synthesis technology applied under microgravity environments and make clear the effect of microgravity on high-temperature composites obtained by combustion synthesis.

1 INTRODUCTION

A novel processing of high-temperature materials, referred to as combustion synthesis,[1–3] is characterized by its exothermic and self-sustaining reaction propagation through a mixture of compressed powders, which gives the following advantages to the technology: (1) high-temperature furnace and complex processing equipment are not necessary, (2) energy consumption is greatly reduced, and (3) large quantities of highly pure materials can be rapidly produced. Combustion synthesis mainly consists of two processes; combustion propagation and structure formation of products. The gas or liquid phase thermo-gravitational transportation is considered to affect the combustion propagation rate in the former process, which subsequently affects the latter process. Since such a transportation and fluctuation caused by mass disturbance and heat convection are restrained under microgravity environment (MGE), the propagation rate would be lowered and the products synthesized under MGE can keep the position where they were formed even in gas or liquid phase, thus resulting in a uniform composition distribution of product.

Shteinberg *et al.* have previously performed highly porous material production under a parabolic flight MGE of about 30 s and they could successfully manufacture a more than 95% porous TiC.[4] We have first carried out TiB_2–Al composite combustion synthesis under a free fall MGE for less than 2 s using a capsule dropping from 10 m height. It was confirmed that the lack of mass migration and the improvement of wetting between TiB_2 and Al under MGE might affect the formation of a fine and dense cermet-like structure in the products.[5] These exploratory works have been performed for mainly solid phase products and successfully showed the difference of products obtained under MGE from those obtained in the terrestrial condition.

In order to assess the potential of combustion synthesis technology applied under MGEs and show the effect of microgravity on high-temperature composites formation more clearly, experiments have been carried out under MGEs developing on: a dropping capsule free-fall (FF–MGE) which attains 10^{-4} g ($g = 9.8$ m/s^2) for 10 s; and a plane parabolic flight (PF–MGE) (10^{-2} g for 20 s).

2 MICROGRAVITY CONDITIONS USED IN THE PRESENT WORK

2.1 Free-fall microgravity environment (FF–MGE)

An underground drop shaft of 710 m, constructed in the microgravity experimental facility of Japan

Microgravity Centre (Kamisunagawa, Hokkaido), has been used for attaining a microgravity condition of 10^{-4} g for 10 s. A capsule of double structure, with inner and outer surfaces, is allowed to fall from the ground to a depth of 490 m along the magnetic guide of the shaft. For obtaining microgravity of good quality, the falling speed of the capsule is controlled by jetting air from behind to compensate for the air resistance around the capsule body during the drop. The maximum weight and size of the capsule payload is 1000 kg and 870 mm × 870 mm × 918 mm. In order to absorb the shock caused by the braking, the speed of the capsule was reduced by damping the air compression at around 200 m, through which the acceleration after free-falling is less than 8 g. The typical microgravity level is shown in Fig. 1(A).

2.2 Plane parabolic flight microgravity environments (PF–MGE)

The PF–MGE was formed by reducing the flight speed immediately after about 2 g acceleration zooming from about 7000 m altitude, and the gravity level, less than 2×10^{-2} g, was attained and kept for about 20 s. Then, it was followed by about 1.5 g acceleration, where the flight altitude changed by about 1500 m. Figure 1(B) shows the typical experimental data on the changes of gravity level in the case of the PF–MGE. The gravity level in the PF–MGE fluctuated much more compared to that in FF–MGE.

The dotted curves shown in Fig. 1 are related to the typical temperature changes measured with thermocouples placed at the side wall of sample compacts of the Ti–B–Al combustion synthesis system. Since the combustion velocity was more than 10 mm/s, the reaction propagation could finish rapidly enough within these MGEs.

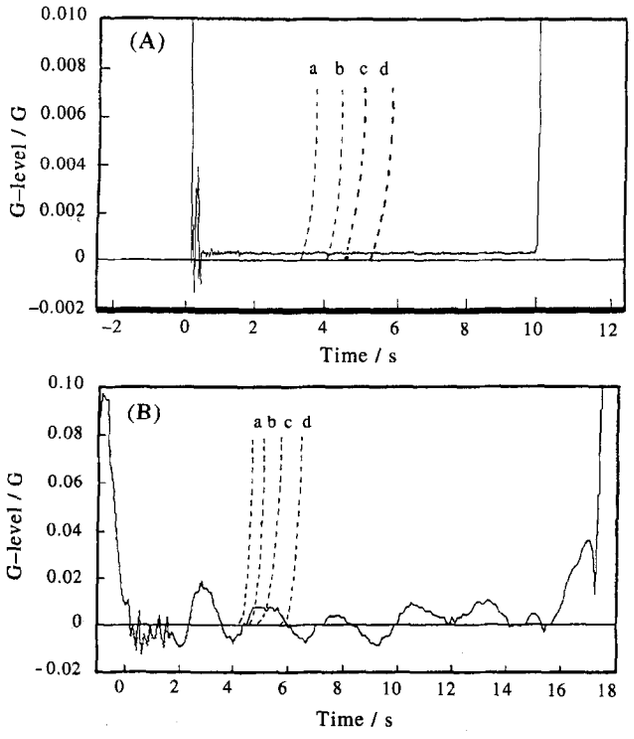

Fig. 1. Typical experimental conditions of gravity level in the FF–MGE (A) and the PF–MGE (B). Dashed line: temperature changes measured with thermocouples set at the side wall of Ti + 4B + Al powder mixture compacts (a–d interval: 30 mm).

3 MICROGRAVITATIONAL COMBUSTION SYNTHESIS OF TiB_2–Al COMPOSITES

The powder mixture of Ti(~50 μm), B(~0.6 μm) and Al(~80 μm) was stoichiometrically blended to comply with the reaction given by:

$$Ti + 4B + Al \rightarrow TiB_2 + 5/6Al + 1/6\alpha - AlB_{12},$$

and pressed to form a compact of 25 mm in diameter, 50 mm in height and 60% in packing density. Four alumel–chromel thermocouples were inserted to the powder compact from its side wall with an interval of 10 mm. Samples were positioned in a stainless steel chamber of 250 mm in diameter (ϕ) and 200 mm in height (h) as shown in Fig. 2(A). The chambers were fixed to a rack in the inner dropping capsule or the plane in order to keep the position during the series of experiments. The reaction was initiated at the beginning of MGE by using electrical heating of a tungsten (W)-filament attached at the end of the sample compact. All experiments were carried out in argon atmosphere. Five experiments were carried out at the same time in the FF–MGE, and two in the PF–MGE.

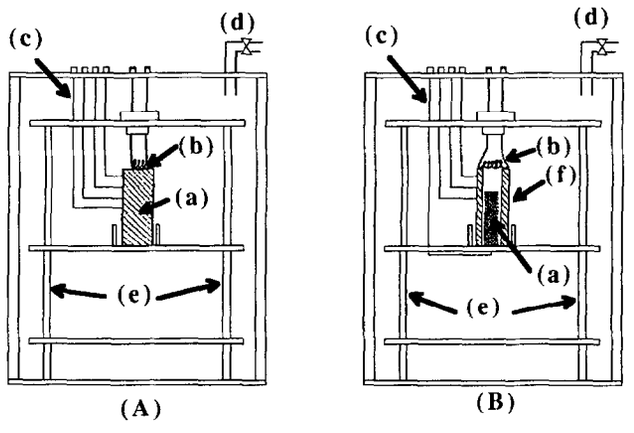

Fig. 2. Reaction chamber for combustion synthesis under the FF–MGE and PF–MGE. (a) Sample compact, (b) tungsten wire, (c) thermocouples, (d) valve, (e) sample holder (with springs in FF–MGE experiments), and (f) chemical oven.

The tendency of the combustion velocity difference for the packing density and the propagation direction was found to be the same, both in the present PF–MGE and ground results, although the values obtained under the PF–MGE are lower than those of ground.[6,7] Therefore, it is considered that heat and gas gravitational transportation affects the combustion propagation. In the FF–MGE, the combustion velocities were 15.5 mm/s and 30.8 mm/s for the systems of Ti + 4B + Al (packing density: 50%) and Ti + 4B (packing density: 50%), which are still rather small compared to those in the PF–MGE.

Compared to the products obtained in the terrestrial condition, the particle distribution seemed to be more uniform when synthesized under the present PF–MGE. The particle size of the products is almost the same as that obtained on ground except that of the product from Ti + 4B powder compact, which is longer in its needle-like structure than that on ground. For both the PF–MGE and FF–MGE, the product morphologies are almost the same. Since the particle size of the products is the same in the direction of reaction propagation in each case, the structure formation process could also complete during these MGEs. As shown in Fig. 3, a somewhat fine composite-layered particle of TiB_2 and Al–AlB_{12}, with about 40 nm layered Al–AlB_{12} surrounding TiB_2 particle of about 0.3 μm, could be found in the case of the PF–MGE. The temperature in the Ti + 4B + Al combustion rises drastically in a short time with the heat of reaction of Ti + 2B and subsequent Al + 2B systems, which reaches more than 2000 K. In the high temperature region behind the combustion front, the co-existence of molten Al–AlB_{12} and solid TiB_2 is expected, and the fine composite layered particle would be formed under the MGE.

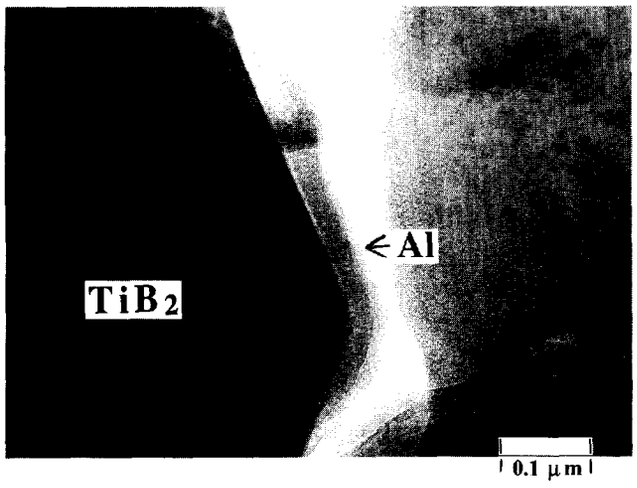

Fig. 3. TEM photograph of the product obtained by combustion synthesis with Ti + 4B + Al powder mixture compact under the PF–MGE.

In the present FF–MGE, a dense cermet-like structure could also be found. The lack of mass migration and the improvement of wetting between TiB_2 and Al under MGE might affect the formation of such a structure. Comparing the PF–MGE and FF–MGE, the amount of Al surrounding TiB_2 in the case of FF–MGE was much higher than that of the PF–MGE, while the aggregation of Al existed in the product on ground and the Al content around TiB_2 particles was much less compared to that in the case of the MGE.[8] It may be that this shows the effect of gravity level on composite formation as the wetting effect is seen more clearly with increasing MGE-level.

4 THERMITE REACTION WITH Ti–B–AL AND Ti–C CHEMICAL OVENS

A product system of ZrO_2–Al_2O_3–Fe has been selected in the present work. The composition has been determined to make the oxide component of ZrO_2–Al_2O_3 in the product be eutectic (42.6 mass% of ZrO_2 in ZrO_2–Al_2O_3 system). Therefore, the mole ratios of thermite and oxide–metal mixtures were $Zr:Al:Fe_2O_3 = 1:3.24:2.29$ and $ZrO_2:Al_2O_3:Fe = 1:1.62:4.58$, respectively. The samples were prepared by packing the above powder mixtures (about 1 g) in Ta tubes (8 mm (ϕ)×0.8 mm (t)×25 mm (h)) and setting the tubes in the Ti + 4B + Al (22.4 g) and Ti + C (28.0 g) powder mixture compacts (60% of packing density) of 25 mm (ϕ)×30 mm (h) cylindrical shape, with 10 mm (ϕ) hollow part, respectively. The sample was positioned in a stainless steel chamber of 250 mm (ϕ)×200 mm (h) (see Fig. 2(B)). The reactant reaction was initiated with the electrical heating of a W-filament attached at its end. All experiments were carried out in argon atmosphere.

Since the induction temperature of the present thermite reaction, $Zr + 3.25Al + 2.29Fe_2O_3$, was about 700 K, the thermite reaction could be induced under MGE by its heating with the Ti + 4B + Al combustion reaction. To attain the full utilization of the present short-time MGE, the delay time of ignition and the temperature hysteresis of the hollow part formed in the cylindrical compacts of Ti–B–Al and Ti–C systems have been preliminary measured on ground. Although the calculated adiabatic temperatures of Ti + 4B + Al and Ti + C combustion are about 2900 K and 3400 K, the maximum temperatures at the inner hollow parts were about 1300 K and 1800 K, respectively. By estimating the interval to reach the

optimum temperature, the starting time for the chemical ovens could be determined. In the present work, the melting point of ZrO_2 + $1.62Al_2O_3$ + 4.58Fe was about 1750 K. Then, the starting time of circularizing the filament current was controlled under the consideration of the delay time of induction and temperature changes in the hollow part during the reaction propagation; the time was about 10 s before PF–MGE reached.

In Fig. 4, the typical X-ray diffraction patterns of the products are shown for the present four cases; the products from the thermite reaction under PF–MGE (A) and on ground (B), and from the melting of the same composition mixture as the product of thermite reaction under PF–MGE (C) and on ground (D). Although it had been expected that the Fe would uniformly distribute in the product

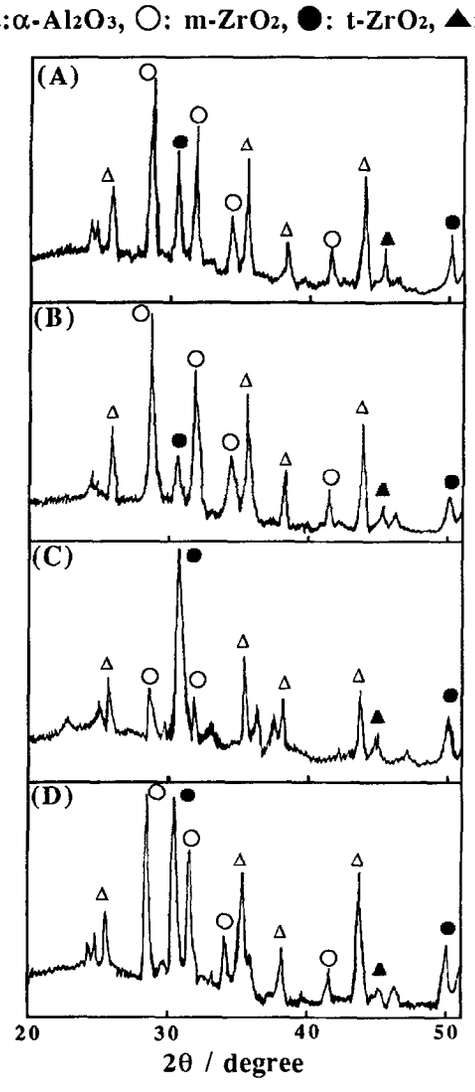

Fig. 4. X-ray diffraction patterns of ZrO_2–Al_2O_3–Fe system products obtained with the aid of the chemical ovens: thermite reaction product under PF–MGE (A) and on the ground (B), melting/solidification product under PF–MGE (C) and on the ground (D).[9]

obtained under MGE, it was confirmed in the present results only that the Fe, which was segregated in the product obtained on ground, was not macroscopically segregated in the products under MGE. The peculiar difference was confirmed in the ZrO_2 phases; the ratio of the tetragonal phase (● mark in the figure) and monoclinic one (○) was quite different between the cases of MGE and ground. Since the tetragonal phase is stable at high temperatures, this may mean that no heat convection under PF–MGE resulted in a high decrease of temperature under PF–MGE. In the case of Zr–Al–Fe_2O_3, excess heat could exist in the product through its self-propagating reaction. Therefore, the cooling rate of the sample was lower than that melted by the Ti+C chemical oven, resulting in lower ratio of tetragonal phase. These results may lead the combustion synthesis application as a chemical oven to a microscopically rapid cooling technique under MGE. Fractured surfaces of the products obtained from the thermite reaction and the melting under the PF–MGE were quite different from those obtained on the ground, especially in their distribution and particle formations. Under PF–MGE, more uniform distribution and finer particles of ZrO_2 could be attained, which would be caused from no disturbance from mass migration. Although both micrographs of the products obtained on ground are almost the same, it could be found that the ZrO_2 particles observed in the product by the melting/solidification process under MGE are much finer, even when compared to those from the thermite reaction under MGE. Such fine particles may have caused the high ratio of ZrO_2 tetragonal phase.

We have also carried out the experiments of microgravitational combustion synthesis with a TR-IA #3 sounding rocket launched on 17 September 1993. The microgravity level during the experimental time of 360 s was less than 10^{-4} *g*. The rocket lifted off from the Space Centre of NASDA (Tanegashima, Kagoshima). The sample arrangement in this sounding rocket parabolic flight experiment (SR–MGE) was different from the cases of FF–MGEs and PF–MGEs. The combustion synthesis was initiated with electric furnace heating, and the following five kinds of powder mixture compacts were set in a Ta cartridge [14 mm (ϕ, inner diameter) × 78 mm (inner length) × 2 mm (thickness)]; (A): 3(Zr + 3.24Al + $2.29Fe_2O_3$) + (ZrO_2 + $1.62Al_2O_3$ + 4.58Fe), (B): Ti + 4B + Al, (C): 2(Ti + 2B) + (Ti + B), (D): 2(Ti + C) + (Ti + 2B) and (E): ZrO_2 + $1.62Al_2O_3$ + 4.58Fe. The packing densities of the compacts (A) – (E) are 57%, 70%, 56%, 60% and 50%, respectively. The Ta cartridge was then

positioned in an isothermal furnace. The reaction of compact (A) was initiated at about 850 K by the heat from the furnace, and the reaction of (B) is subsequently initiated and self-propagated with the help of the reaction heat of (A), followed by the reaction propagation of (C) and (D). The adiabatic temperature of the reaction in (D) is more than 3400 K, so that compact (E) melts and solidifies during the present 360 s SR–MGE.

The morphologies of ZrO_2–Al_2O_3–Fe composite products obtained by combustion synthesis of (A) and melting/solidification of (E) under the present MGE are quite different from those obtained in the related terrestrial condition, especially in their distribution and particle formations. Under the SR–MGE, more uniform distribution and finer particles of ZrO_2 could be attained, which would be caused from no disturbance from mass migration. In the PF–MGE experiments, it could be found that the ZrO_2 particles observed in the product by the melting/solidification process under MGE are much finer compared to those by the thermite reaction under MGE, resulting in the high ratio of ZrO_2 tetragonal phase. For the present SR–MGE result, the combustion synthesized product has also shown finer ZrO_2 particle distribution, even when compared to that by the melting/solidification process.

The particle size of the TiB_2–Al–B composite products is almost the same as that obtained on the ground. In the high temperature region behind the combustion front, the co-existence of molten Al–AlB_{12} and solid TiB_2 is expected, and the fine composite layered particle would be formed under MGE. In the present MGE, a dense cermet-like structure could also be found. The lack of mass migration and the improvement of wetting between TiB_2 and Al under MGE might affect the formation of such a structure. Compared to the terrestrial results, the amount of Al surrounding TiB_2 in the case of the SR–MGE was much higher.[10] It may be that this shows the effect of the MGE on composite formation as the wetting effect is seen more clearly under the SR–MGE.

5 CONCLUSION

The finely dispersed composite particles of TiB_2 surrounded by Al–AlB_{12} layer could be formed by combustion synthesis of Ti + 4B + Al powder mixture under the present short-time PF–MGEs and FF–MGEs. The combustion velocity of the present Ti–B–Al systems under the present MGEs was smaller than that on the ground. The amount of Al content around TiB_2 particles increased with gravity level decreasing from ground to the PF–MGE → the FF–MGE, which would be caused from the consideration that the wetting between TiB_2 and Al–AlB_{12} at high temperatures becomes remarkable under MGE.

The thermite reaction of the Zr–Al–Fe_2O_3 system and the melting/solidification of the ZrO_2–Al_2O_3–Fe system have been successfully performed with the chemical ovens of Ti–B–Al and Ti–C system combustion synthesis under PF–MGE, respectively. The peculiar difference in the ZrO_2 distribution and its structure was confirmed between the cases of MGE and ground. The ceramic eutectic of ZrO_2 and Al_2O_3 has been investigated, not only for its refractoriness and thermomechanical properties, but also for its structural characteristics following directional solidification. Therefore, the present results would lead to a remarkable evidence of material processing difference under MGE through further detailed investigation of the products.

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