Synthesis of Single Phase La$_2$Zr$_2$O$_7$ by Wet Mechanochemical Treatment*1

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Powders of La$_2$O$_3$ and ZrO$_2$ in ethanol based suspension were used as precursor materials for the wet mechanochemical (MC) synthesis of single phase La$_2$Zr$_2$O$_7$, a promising thermal barrier coating (TBC) material. Lanthania powder was first preheated at 1200°C prior to MC treatment in a planetary ball mill at 200, 300 and 400 revolutions per minute (rpm) milling speeds for 12, 18, and 24 hours using zirconia pot and balls. The slurries were then dried at 110°C for 24 hours in an oven followed by heat treatment at 1500°C for 1 hour. X-ray diffraction results showed that single phase La$_2$Zr$_2$O$_7$ was produced using 5 mm ball at 200 rpm milling for 12 hours and using 10 mm balls at 400 rpm for 24 hours. Smaller grinding balls and slower milling speed allowed more homogeneous mixing during wet mechanochemical treatment in a 250 mL milling pot. The average particle size of the products is lower than 1.8 μm. The yield of powder is greater than 98%.

1. Introduction

Thermal barrier coatings (TBCs) have found very significant application in power generating gas turbines, improving thermal efficiency due to increase in the inlet temperature. Selection of which however, is restricted by some basic requirements: (1) high melting point, (2) no phase transformation between room temperature and operation temperature, (3) low thermal conductivity, (4) oxidation resistant, (5) thermal expansion match with the metallic substrate, (6) good adherence to the metallic substrate and (7) low sintering rate of the porous microstructure.1-3 The most popular TBC material currently in use is yttria stabilized zirconia (YSZ). This TBC material however, contains metastable zirconia which leads to destructive transformation on high temperature heating and cooling. Moreover, it is also oxygen transparent, for which reasons alternative TBC materials are being sought.5-7

Recently, lanthanum zirconate La$_2$Zr$_2$O$_7$ having a cubic pyrochlore structure has been discovered as a promising TBC material due to its very high thermal stability, high melting point, low sintering, low thermal conductivity and not oxygen transparent.5 Such discovery has led to widespread researches on its synthesis including mechanochemical (MC) treatment which uses mechanical energy to induce chemical or physiochemical transformation.5-7

Previous dry MC synthesis of lanthanum zirconate powders used high energy milling which encountered obstacles due to powder agglomeration at the sides of the milling pot and yielded only less than 40% synthesized powder.5-8 Previous studies on wet MC treatment yielded higher amount of powder but required about 24 hours high energy milling followed by 12 long hours of heat treatment at 1400°C.9,10 Compared with the dry milling process, wet milling has the advantages of good homogenization, low power requirement, no dust problems, higher rotational speeds, smaller particle size than dry and compatible with spray drying and casting processes.11 Thus, the main objective of this study is to synthesize single phase La$_2$Zr$_2$O$_7$ employing wet mechanochemical treatment in a planetary ball mill at lower operating time and energy compared to the previously published MC syntheses. This method of synthesis has the advantages of shorter synthesis time and fewer variables to control compared to the co-precipitation method and manual mechanochemical synthesis by hand which require long hours of chemical reaction and subsequent heat treatment.

2. Experimental Procedure

Powders of La$_2$O$_3$ (High Purity Chemicals, 99.9%) and ZrO$_2$ (Tosoh, 99%) were used as precursor materials. The average particle size for La$_2$O$_3$ is 5 μm while for ZrO$_2$ is 3.4 μm. Preheating of La$_2$O$_3$ powder at 1200°C for 2 hours to remove the hydroxide components was carried out immediately before weighing. An ethanol based suspension was then prepared with La$_2$O$_3$ and ZrO$_2$ powders in their stoichiometric amounts. It was followed by wet MC treatment in a planetary ball mill (Fig. 1) initially at 400 rpm milling speed with increasing milling time based from the best results of the previous synthesis6-8 using a 250 mL zirconia pot and balls. Two mixtures were prepared using grinding balls of 5 and 10 mm diameter. The ball to powder ratio was equal to 10:1. The slurries were then dried at 110°C for 24 hours in an oven then heat treated at 1500°C for 1 hour in air. The average particle size of MC treated powders was determined by a conventional laser particle size analyzer (Sympatec Helos System). The dried powder was first dispersed by a jet

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Fig. 1 Schematic diagram of the experimental set-up in a planetary ball mill.
blasting attachment apparatus (Rodos) to overcome the adhesive forces between the particles before being fed into the particle size analyzer. The structural analysis on the phase transformation of the products was performed using XRD (Philips), while the morphological transformation was investigated using FE-SEM (Jeol). After the results were evaluated for these milling conditions, wet MC treatment was also performed at 200 and 300 rpm for 12 hours using the different sizes of grinding balls in separate mixtures. The purpose of this procedure is to determine the possibility of mechanochemical synthesis at lower operating time and energy. Similar product analyses as of the first milling condition were employed.

3. Results and Discussion

3.1 Particle size analysis

Primarily, the effect of mechanochemical treatment on the starting powders is size reduction which eventually leads to an increase in material reactivity. The average particle sizes of the powders generated after wet MC treatment are lower than 1.8 \( \mu m \) which is far smaller than the average particle size of the starting powders (ZrO\(_2\), 3.4 \( \mu m \) and La\(_2\)O\(_3\), 5 \( \mu m \)). The average particle size of the starting powders decreased after 12 hours of planetary milling. With the decrease in particle size, brittle fracture which is an elastic behavior of the particles decrease and their plastic deformation increase, and the grindability limit is reached. This is the limit where the powder particles change their shape rather than being reduced in size by fracture due to further grinding. As shown in Fig. 2, after milling time of 12 hours and milling speed faster than 200 rpm, the values of the average particle size of the powders tend to fluctuate. Particles size becomes independent from milling speed and milling time. At this point the particles start to agglomerate which results to ineffective grinding brought about by the particle coalescence from the transformation of deformation mechanisms from the elastic to plastic region as previously explained.

A few specks of powder which agglomerated to the sides of the container during drying were difficult to remove. Thus, powder recovery for all samples resulted to approximately 98%. However, compared with the previous results in dry MC treatment which yielded less than 40%, the present result is far more industrially significant.

3.2 Phase transformation

The effect of wet MC treatment at 400 rpm with increasing milling time using 5 mm and 10 mm zirconia balls and subsequent heat treatment at 1500°C on the structure and texture of the starting powders is shown in Fig. 3. After the wet MC treatment, new phases of La(OH)_3 were transformed from the raw mixtures of the starting powders. Gradual disturbance in the crystal structure for detected free La\(_2\)O\(_3\) and ZrO\(_2\) was manifested by the decrease in the intensity of the diffraction line after milling relative to the raw mixture of the starting powders. The presence of weak and broad peaks in the XRD patterns reveal the formation of amor-
phous-like structure of the powders after milling. After heat treatment at 1500°C for 1 hour, the low intensity peaks of the milled powders were transformed into very narrow high intensity peaks of crystalline lanthanum zirconate. The results show that when 5 mm balls were used at 400 rpm (Fig. 3(a)), even at prolonged milling time followed by heating at 1500°C for 1 hour, still single phase lanthanum zirconate was not formed. A few low intensity free oxides of lanthanum relative to the major peak at (222) were still detected. This indicates the incompatibility of the milling condition using small grinding balls and too fast milling speed in a small grinding pot like 250 mL in grinding an ethanol based suspension of La$_2$O$_3$ and ZrO$_2$ powders. Too fast milling would cause the mill charge to be carried right to the top of the circular motion during milling and do not fall but continue round on the wall of the mill such that no grinding occurs at all. This happens when the operational milling speed goes near and beyond the critical speed of grind which is dependent only on the diameter of the milling pot. The number of peaks for free La$_2$O$_3$ detected however, decreased with increasing milling time. Single phase La$_2$Zr$_2$O$_7$ was only synthesized after 24 hours of wet MC treatment using 10 mm zirconia balls and subsequent heat treatment at 1500°C. All the peaks in Fig. 3(b) for such milling condition matched with the JCPDS Card PDF No. 71-2623 for lanthanum zirconate. With smaller grinding media and slower milling speed, greater homogeneous mixing and reaction between particles occurred, as evidenced by the formation of single phase lanthanum zirconate at 200 rpm for 12 hours with 5 mm grinding balls than with 10 mm balls. This result gave the lowest synthesis time and energy than with the initial milling condition used in the present study and in the other previously published methods of La$_2$Zr$_2$O$_7$ synthesis using wet MC treatment. This is relatively the best optimized milling condition for the wet MC synthesis of single phase La$_2$Zr$_2$O$_7$ in a 250 mL zirconia milling pot. At faster milling speed than 200 rpm, it can be noticed that more peaks of free La$_2$O$_3$ are present even after heating at 1500°C for 1 hour, indicating lesser reaction between particles during milling and resulted to lower particle reactivity during heating. Thus, in every milling practice, it is always important to consider all the factors affecting the efficiency of milling which are: (1) speed of mill; (2) quantity of balls; (3) size of balls; (4) quantity of material; (5) consistency of material by wet grinding; and (6) initial particle size. These factors are dependent on each other and must be carefully considered during optimization of any milling procedure to achieve the best mixing and reaction conditions desired.

3.3 Morphological transformation

The transformation of particle morphology was also investigated using FE-SEM. Photo micrographs reveal the morphological transformation of the raw powders (Fig. 5) into single phase lanthanum zirconate can also be formed at 200 rpm for minimal 12 hours using 5 mm zirconia balls and subsequent heat treatment at 1500°C for 1 hour. All the XRD peaks in Fig. 4(a) of lanthanum zirconate synthesized using such milling condition also matched with JPDS Card PDF No. 71-2623. With smaller grinding media and slower milling speed, greater homogeneous mixing and reaction between particles occurred, as evidenced by the formation of single phase lanthanum zirconate at 200 rpm for 12 hours with 5 mm grinding balls than with 10 mm balls. This result gave the lowest synthesis time and energy than with the initial milling condition used in the present study and in the other previously published methods of La$_2$Zr$_2$O$_7$ synthesis using wet MC treatment. This is relatively the best optimized milling condition for the wet MC synthesis of single phase La$_2$Zr$_2$O$_7$ in a 250 mL zirconia milling pot. At faster milling speed than 200 rpm, it can be noticed that more peaks of free La$_2$O$_3$ are present even after heating at 1500°C for 1 hour, indicating lesser reaction between particles during milling and resulted to lower particle reactivity during heating. Thus, in every milling practice, it is always important to consider all the factors affecting the efficiency of milling which are: (1) speed of mill; (2) quantity of balls; (3) size of balls; (4) quantity of material; (5) consistency of material by wet grinding; and (6) initial particle size. These factors are dependent on each other and must be carefully considered during optimization of any milling procedure to achieve the best mixing and reaction conditions desired.

Fig. 4 X-ray diffraction profiles for the phase transformation of La$_2$O$_3$ and ZrO$_2$ powders into La$_2$Zr$_2$O$_7$ after wet milling for 12 hours with increasing milling speed using (a) 5 mm and (b) 10 mm zirconia balls and subsequent heat treatment at 1500°C.
larger particles of lanthanum zirconate of well defined particle boundaries upon heat treatment at 1500°C for 1 hour. Smaller grinding balls (5 mm) and relatively slower milling (200 rpm) allowed more homogeneous mixing and increased particle reactivity than with larger balls (10 mm) and faster milling (400 rpm). This is therefore, relatively the best optimized milling condition for the wet MC synthesis of single phase La$_2$Zr$_2$O$_7$. The average particle size of MC treated powders is less than 1.8 µm. The yield of powder is greater than 98% which is much higher compared to the previous dry MC treatment results. The advantage of lower synthesis time and energy as compared to the previous mechanochemical treatment procedures, has made the present method a more efficient one for the synthesis of single phase lanthanum zirconate thermal barrier coating material.

4. Conclusion

The synthesis of single phase La$_2$Zr$_2$O$_7$ by wet mechanochemical treatment was successfully conducted at minimal 200 rpm for 12 hours using 5 mm zirconia balls and at 400 rpm for 24 hours using 10 mm zirconia balls followed by heat treatment at 1500°C for 1 hour. Smaller grinding balls (5 mm) and relatively slower milling (200 rpm) allowed more homogeneous mixing and increased particle reactivity than with larger balls (10 mm) and faster milling (400 rpm). This is therefore, relatively the best optimized milling condition for the wet MC synthesis of single phase La$_2$Zr$_2$O$_7$. The average particle size of MC treated powders is less than 1.8 µm. The yield of powder is greater than 98% which is much higher compared to the previous dry MC treatment results. The advantage of lower synthesis time and energy as compared to the previous mechanochemical treatment procedures, has made the present method a more efficient one for the synthesis of single phase lanthanum zirconate thermal barrier coating material.

REFERENCES

7) N. Fujisawa: MS Thesis (Tohoku University, Japan, 2003).