Journal of the European Ceramic Society 23 (2003) 765–772

www.elsevier.com/locate/jeurceramsoc

Processing of mullite–molybdenum graded hollow cylinders by centrifugal molding technique

R. Sivakumar[a,*], T. Nishikawa[a], S. Honda[a], H. Awaji[a], F.D. Gnanam[b]

[a]*Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan*
[b]*Anna University, Chennai 600 025, India*

Received 17 August 2001; received in revised form 31 May 2002; accepted 16 June 2002

Abstract

Continuous microstructural graded hollow cylinders were processed and characterized using a developed technique named centrifugal molding technique. Alcohol based slurries containing mullite and molybdenum (Mo) powders were tested in this work. Hollow cylinders with ceramic rich in inner surface and metal rich in outer surface were fabricated with the smooth increase of Mo content toward outer direction. Sintering condition was optimized and graded hollow cylinders were sintered at 1600 °C for 3 h in the reducing atmosphere. No new phases were observed after sintering. Microstructural observation and EDX analysis performed showed linear gradation of Mo content along the radial direction of cylinders. The methodology of mixing process of starting materials in the form of slurry immensely influenced the microstructural pattern across the thickness of graded specimens. Measured Vickers hardness values proved the continuous compositional change from inner to outer surface of graded cylinders and the hardness became constant in outer surface of graded specimens due to formation of interconnected Mo structures.

Keywords: Centrifugal molding; Functionally graded material; Hardness; Microstructure-final; Mullite

1. Introduction

Functionally graded materials (FGMs) are new versions of composite materials that are microscopically inhomogeneous in unique characterization. The composition varies gradually and continuously, or, stepwise, from ceramic to ceramic or ceramic to metal. This variation of microstructure distinguishes FGMs from conventional composite materials and the compositional variation across the cross-section resulting in unique physical properties.[1] These characteristic microstructures are expected to reduce the thermal stress at the interfaces, thus developing the thermal shock resistance properties. In the application side, these materials generally have the advantage in which requirements for the properties differ at opposite end and are used in severe environments where the temperature gradient is steep such as in rocket nozzles and turbine components.

Various fabrication methods are applied in recent for the preparation of bulk FGMs and graded thin films. Some of the prevailing techniques used in practice to fabricate FGM includes layered technique,[2–4] sequential slip casting technique,[5] centrifugal casting technique,[6–9] slip casting[10–12] for bulk graded materials and chemical vapor deposition,[13] plasma spraying,[14,15] electrophoretic deposition[16–18] for graded films. Among the methods for preparing bulk FGMs, the centrifugal casting technique is the most economical method for producing continuous change in composition through the thickness of component. The process involves the addition of reinforcing particles to the molten metal and centrifuged at higher velocities to get the graded compositional change along radial direction and then solidify to preserve the gradation. A thick walled ring of SiC/Al FGM was fabricated by a centrifugal casting technique.[6]

With a similar principle of centrifugal casting technique, a newer technique named centrifugal molding technique is being developed by Nishikawa et al.[19] and Sivakumar et al.[20] for the fabrication of continuous graded ceramic/metal hollow cylinders. In this technique,

* Corresponding author. Tel.: +81-52-736-7219; fax: +81-52-736-7224.

E-mail address: rsivakumar@email.com (R. Sivakumar).

0955-2219/02/$ - see front matter
PII: S0955-2219(02)00197-8

Table 1
Properties of the starting materials

Properties	Mean particle size (μm)	Melting point (°C)	Density ($\times 10^3$ kg/m^3)	Modulus of elasticity (GPa)	Thermal expansion coefficient at room temperature (10^{-6}/K)
Mullite	1.3	1810	3.17	225	4.8
Molybdenum	3.0	2610	10.22	330	4.9

the centrifugal force enables the ceramic powder mixed with metal powder to create a gradient compositional distribution due to the difference in their material densities and particle sizes.

This work primarily concerns about developing and characterizing continuous graded FGM hollow cylinders fabricated by centrifugal molding technique. In this present work, mullite and molybdenum (Mo) were taken as the raw materials. Since the large difference in densities of ceramic and metal (3170 kg/m^3 for mullite and 10220 kg/m^3 for Mo), it is convenient to fabricate mullite–Mo FGMs by the centrifugal molding technique, which creates the compositional gradient in radial direction. They are ideal candidates for preparing FGMs since they have similar thermal expansion coefficients (4.8×10^{-6} K^{-1} for mullite and 4.9×10^{-6} K^{-1} for Mo), thus reducing the residual stresses without any thermal expansion mismatch and reacting each other at high temperatures. Mo is a good electrical and thermal conductor, whereas, mullite is an electrical insulator and has low thermal conductivity. This opens a large number of possible applications in electronics, in thermal barrier coatings or in electrical conductor/insulator component.[21]

2. Experimental procedure

2.1. Starting materials

The following commercially available micrometer sized powders were used for this work: (i) mullite (Kyoritsu Yogyo Co., KM102) with mean particle size of 1.3 μm, specific surface area 8.7 m^2/g, and Mo (Mitsuwa's Pure Chemical Co.) with mean particle size of 3.0 μm. The properties of the starting materials are shown in Table 1.

2.2. Processing

Fig. 1 summarizes the processing route used in this work for the fabrication of continuous graded hollow cylinders. Mullite and 40 vol.% of Mo mixture was prepared by wet mixing in polyethylene pot with ethanol for 24 h. MgO was added in small quantity of 0.5 wt.% of mullite[22] as the sintering aid for the better densification. Uniformly sized alumina balls were added for homogenous wet mixing. The slurry was dried for 24 h at 110 °C. Dried composite powders were then ground in high purity alumina mortar and passed through screen having the aperture size of 350 μm. Stable slurry of high solid content was then prepared by uniform mixing of pre-mixed composite powder with ethanol as solvent by magnetic stirrer for 1 h. Poly vinyl butyral (PVB) and Dolapix ET 85 (Zschimmer & Schwarz GmbH & Co.) were also added along with the slurry as binder and dispersant, respectively. A small amount of PVB was added to enhance the green strength during handling. Dolapix ET 85 is a commercially available dispersant which is a carbonic acid ester, alkali free polyelectrolyte used as an organic dispersant and deflocculant for oxide bodies. The density of the dispersant is

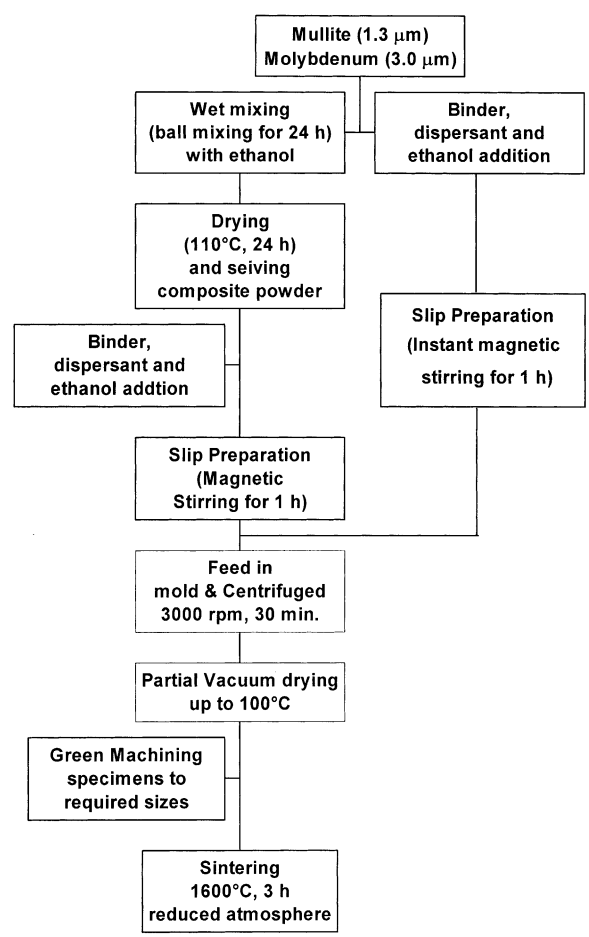

Fig. 1. Processing diagram for FGM hollow cylinder fabrication.

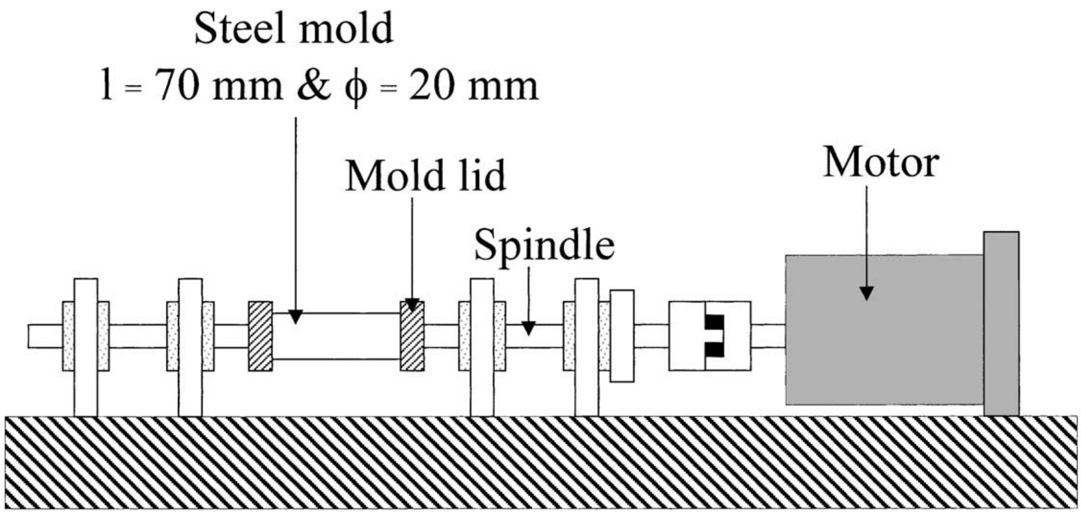

Fig. 2. Schematic representation of experimental setup for fabricating graded hollow cylinder.

1140 kg/m^3 at room temperature with pH of 7.0 and active matter of 65% in weight. These binder and dispersant are completely soluble in alcohol and are added in the amount of 0.5 wt.% to each slurry.

Slurry containing 40 vol.% of Mo and mullite was also prepared using instant mixing of starting materials with same concentrations of additives and solvent by magnetic stirrer for a period of 1 h. The percentage of solids in slurries of mullite and Mo was maintained at 23% by volume through the experiment. The slurry prepared by different mixing procedures was poured in steel mold with the inner diameter of 20 mm. For easy removal of the sample after forming, the inner surface of mold was coated previously with a solution of vaseline which acts as lubricant. The cylindrical steel mold was centrifuged along the radial direction with a speed of 3000 rpm for 0.5 h. The device setup is shown as in Fig. 2. After centrifugation, the residual liquid was poured out and the mold with sample was dried in vertical position inside vacuum chamber at room temperature for 24 h. The temperature was allowed to rise to 100 °C with a ramp of 5 °C/h. The dried and shrunk sample could be removed from the mold easily. The green tube had an approximate dimension of 7.5 mm in thickness and 70 mm in length. The sample was cut and then machined at desired length for the sintering and the following characterization. Machined sample was sintered on flat ceramic substrate at 1600 °C for 3 h in an atmosphere of H_2/N_2 with H_2 of 4% and rest N_2. The heating and cooling rate was taken as 200 °C/h through sintering process.

2.3. Characterization

The bulk densities of sectioned and sintered graded hollow specimens were measured by Archimedes method with distilled water as a media. The microstructures of the sintered specimens were observed on the cross-sectioned surfaces, cut perpendicular to the longitudinal axis of the hollow cylinders using a scanning electron microscope (ABT-55) equipped with energy dispersive X-ray (EDX) analysis system. Specimens were polished up with the diamond abrasive slurry of 3 μm prior to the microstructural inspection. Microstructures were taken in equal intervals of distance of 0.6 mm, with 3.0 mm being the thickness of the sintered graded hollow cylinders. The compositional change along the radial direction was examined by EDX area analysis, which was performed at equal distances from the inner to the outer direction of specimens. Vickers hardness was also measured in the polished surface along radial direction with the given load of 9.8 N in equal interval of distance to confirm the compositional change.

3. Results and discussion

3.1. Processing

Continuous graded hollow cylinders were fabricated with the centrifugal molding technique using ethanol as the solvent. Due to the centrifugal force enabled and the large difference in densities of starting materials (3170 kg/m^3 for mullite and 10220 kg/m^3 for Mo), a gradient compositional distribution was created along the radial direction in the specimen. Earlier studies showed that the mullite and Mo particles coagulated in water based slurries, while the slurries having ethanol remained deflocculated. The two reasons behind are that the pH of mullite suspension (6.1) is near to the isoelectric point of mullite (6.03) and molybdenum oxide on the surface partially dissolute in water. This partial dissolution decreases pH in slurry to 4.1. At this pH, mullite particles are getting attracted with Mo and thus coagulation occurs.[23] Considering these surface chemistry, the alcohol-based slurries were taken in our studies.

The centrifugal time was taken as 30 min and the residual liquid was poured out after the first 15 min and again centrifuged for 15 min. Kim et al.[24] reported the repeated centrifugal casting of monolithic alumina tubes with a rotating speed of 2500 rpm. It was then concluded that the repeated centrifugal casting of alumina slurries used had the fine and uniform microstructures.

After centrifuging process, cracks were formed during drying in the air atmosphere along the axial direction of the specimens. It was then optimized by drying in the vacuum chamber for 24 h in partial vacuum. Thus, the evaporation of ethanol in the graded specimens is quite rapid and the sample gets dried in a faster rate avoiding drying cracks. Temperature increased in the partial vacuum stage with slow heating rate of 5 °C/h made samples shrink and detached easily from the mold.

3.2. *Effect of sintering environment*

Since the Mo is easily oxidized in air atmosphere, the reduced atmosphere or high vacuum is necessary for sintering Mo containing samples. Sivakumar et al.[25] sintered mullite/Mo composites in high vacuum of 4.5×10^{-5} Torr using a pulse electric current sintering (PECS) technique. No oxide of Mo was observed after sintering by X-ray diffraction analysis. Graded hollow cylinders could not be sintered by PECS technique under the uniformly applied pressure during sintering, and hence the optimum sintering condition has to be identified. Thermo gravimetric analysis (TGA) of different grain sized Mo powders in various atmospheric conditions up to 600 °C are shown in the Fig. 3. From the figure, it can be seen that the weight gain of Mo powder sized 3 μm started around 285 °C in air atmosphere and had a weight gain of 50% at 600 °C. On the contrary, in argon atmosphere, the weight gain started at around 330 °C and had a weight gain of only 1.7% at 600 °C. The results indicate that the weight gain of Mo powder is large in air atmosphere, which in turn reveals the oxidation of Mo. Oxidation of Mo powders was insignificant, but little in argon atmospheres compared with that of air atmosphere. The oxidation of Mo powders in argon atmosphere can be explained as that the oxygen partial pressure may be slightly higher than the equilibrium pressure for the conversion into MoO_2.

TGA results of Mo powders in N_2/H_2 atmosphere proposed by Ishibashi et al.[26] have shown that there is weight loss of 2 wt.% around 600 °C. The weight loss was explained due to reduction of Mo oxide present in layer of powder and the partial pressure of oxygen was low enough to reduce MoO_2 to Mo. Therefore, the graded hollow cylinders were sintered in H_2/ N_2 atmosphere with 4% of H_2 and N_2 of 96% at 1600 °C for 3 h. XRD analysis showed no oxide peaks in the sintered samples.

The sintered graded hollow cylinders had a relative density of around 80% of theoretical densities prepared by both processing routes. This decrease in the sintered densities may be due to insufficient centrifugal force during centrifugation at a speed of 3000 rotations per minute and/or due to smaller diameters of the mold (20 mm). Works have been proceeded with increased rotational speeds and with larger diameter of mold for various ceramic/metal and ceramic/ceramic systems to improve the sintered densities.

3.3. *Microstructure and composition*

The sintered samples had mullite rich regions at the inner side and Mo rich regions in the outer side of FGM cylinders [Fig. 4]. Fig. 5(a) shows the electron micrographs of polished surface of graded hollow cylinder

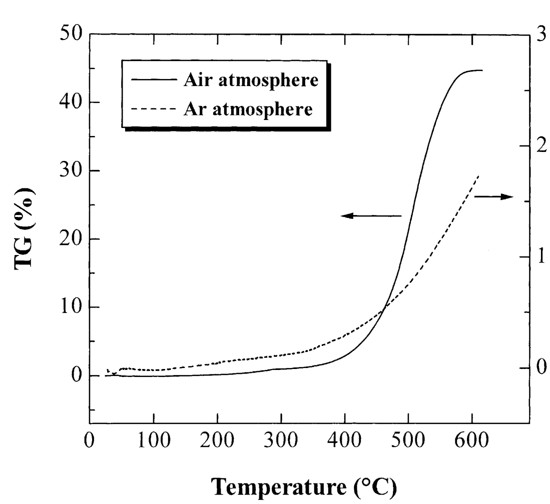

Fig. 3. Thermograms of 3 μm sized Mo powders in air and argon atmospheres.

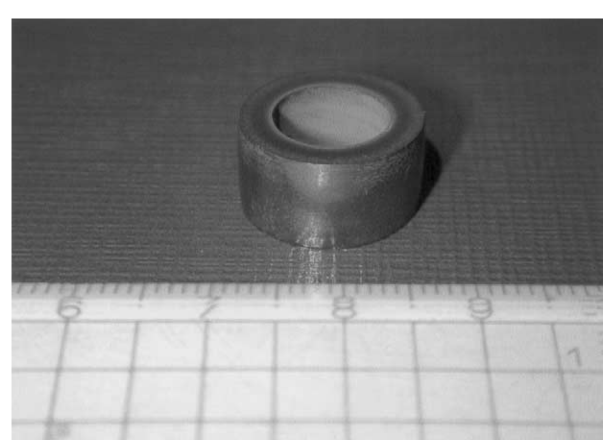

Fig. 4. Mullite/Mo FGM hollow cylinder by centrifugal molding technique.

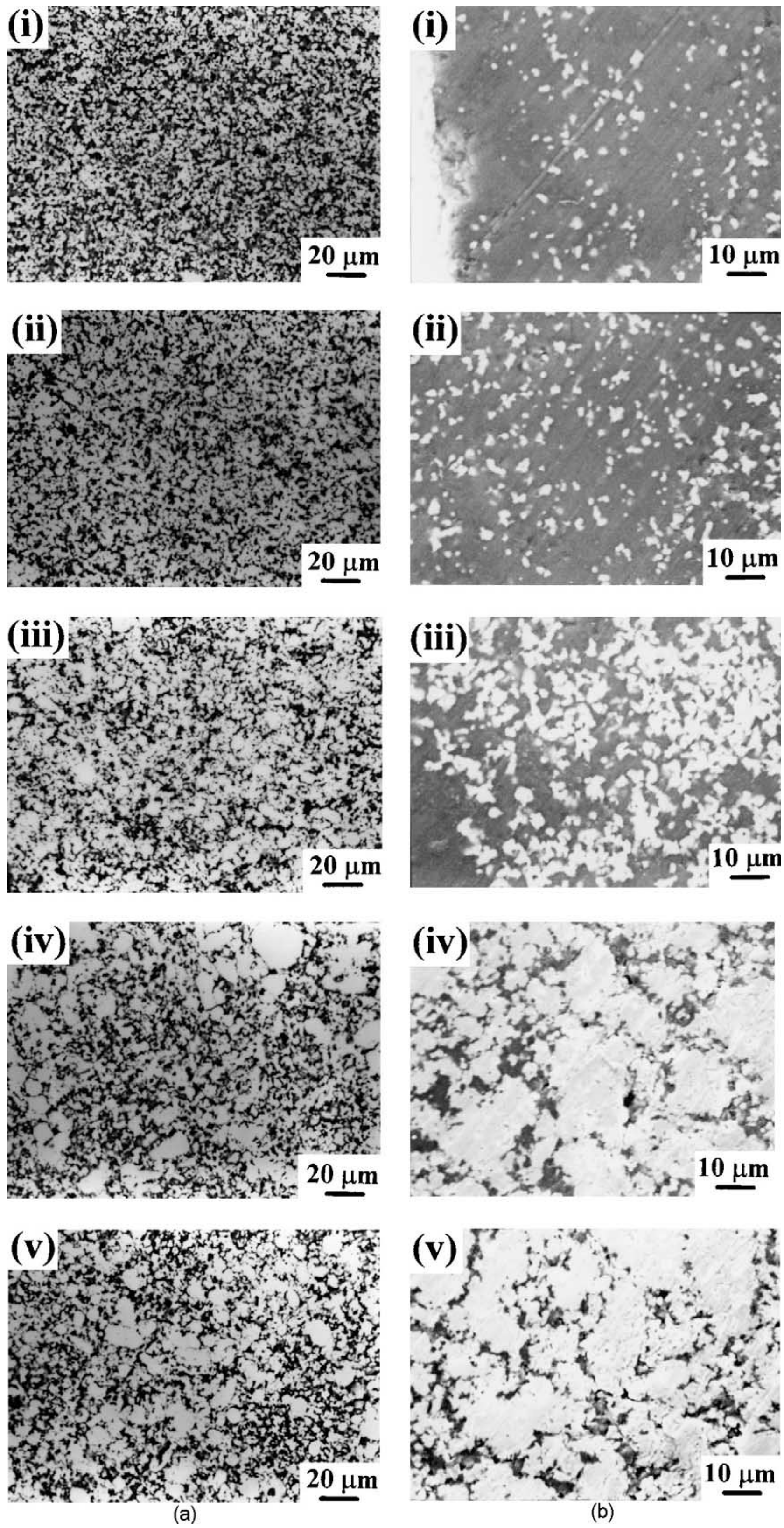

Fig. 5. Electron micrographs of mullite–40 vol.% Mo FGM hollow cylinders by (a) pre-mixed composite powder; (b) instant stirrer mixing of starting materials.

containing 40 vol.% Mo and mullite prepared by stirrer mixing of pre-mixed composite powder with solvent and other additives. In these micrographs, the Mo particles appear as bright phase. The microstructure locations are represented from the inner surface towards outer side of the graded hollow cylinder. The results indicate that Mo is relatively distributed and gradation was present from the inner side of the hollow cylinder towards the outer direction when observed at equal intervals of distances across the hollow cylinder. Larger Mo particles, due to the centrifugal force, were observed on the outer side of the graded hollow cylinder. From the micrographs, it can be seen that Mo particle concentration is high even in the mullite rich region, while interconnected Mo structures were present in metal rich region, that is, on the outer surface of graded cylinders. Various binder concentrations were tried out to optimize the gradient of Mo along the radial direction from inner towards outer side. Mo concentration was high in the center of the FGM hollow cylinder when the binder concentration was increased from 0.5 to 1.0 wt.%, in turn, increasing the viscosity of mullite–Mo composite slurries. The graded behavior mainly depends on the viscosity of the slurry.

Microstructures of 40 vol% Mo graded hollow cylinder centrifuged with slurry prepared by instant stirrer mixing of starting materials and additives is shown in Fig. 5(b). The microstructural pattern is differed here from the graded cylinders fabricated with the slurries containing pre-mixed composite powders [Fig. 5(a)]. From the micrographs in Fig. 5(b), it can be seen that the molybdenum grains are isolated in the mullite rich region and its concentration gets increased towards the outer surface regions. Also, the microstructures in the outer surface regions showed high contents of Mo with interconnected structure.

The microstructures of graded hollow cylinders reveal that the methodology of slurry preparation has a vital influence on the gradation of Mo along the radial direction. From Fig. 5(a) and (b), it can be seen that there is a smooth change in the composition through the thickness for the FGM hollow cylinders prepared from instant stirrer mixing of starting materials than the graded cylinders prepared from stirrer mixing of pre-mixed composite powders. Also, the adherence between the starting materials is minimal in instant stirrer mixing of slurry and the Mo particles are isolated in the inner surface of graded specimens.

The variations in the compositional profile across the graded specimens in turn varying the material properties reduce the thermal stresses produced due to severe thermal shock environments. The numerical analysis of temperature and stress distributions in graded hollow cylinder composed of mullite and molybdenum is discussed briefly elsewhere.[27] The analytical results proved that mullite–Mo graded hollow cylinders released the thermal stresses on the ceramic surface considerably as well as in metallic surface. Also, compressive stresses were present after thermal shock and no tensile stresses were found when the severity of quenching medium is varied. In this mullite–Mo system, the thermal residual stresses produced during the cooling of sintered specimens are minimal due to smaller thermal expansion mismatch.

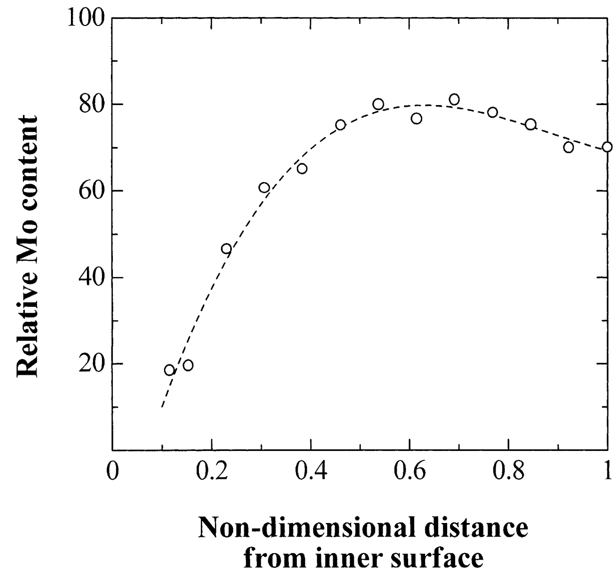

Fig. 6. Compositional analysis of relative Mo content in 40 vol.% Mo FGM graded cylinder.

EDX compositional analysis was performed along with SEM for mullite–Mo FGMs with 40 vol.% Mo content prepared from the pre-mixed composite powders as starting materials (Fig. 6). The relative Mo content increased monotonously from inner surface towards outer side in equal intervals of distance. The average relative Mo content present in the FGM hollow cylinder is given by 70.56 wt.%, which corresponds to 40 vol% in initial composition.

3.4. Hardness

Vickers indentations were placed in the polished surface of graded specimen across the thickness from inner surface towards outer direction. For an indent load of 9.8 N, the hardness was measured in equal intervals of distances. Fig. 7 shows the variation of Vickers hardness of FGM hollow cylinder containing Mo of 40 vol.% and mullite. From the figure, it can be seen that the hardness decreased in a steady manner when measured from inner towards outer side of hollow cylinder. Vickers hardness is nearly 4 GPa in mullite rich region for the specimen corresponding to the microstructures in Fig. 5(a), while the hardness of monolithic mullite being 15 GPa. The decrease in the hardness values may be due to the co-existing of Mo particles in the centrifuged hollow FGM cylinders. It is speculated that mullite

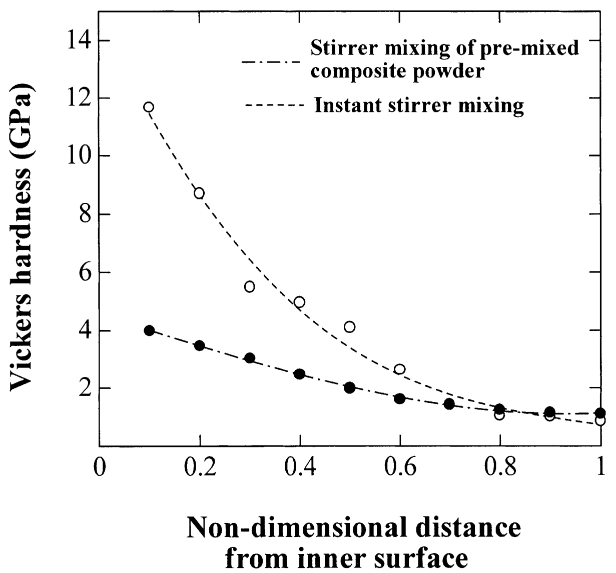

Fig. 7. Variation of Vickers hardness of 40 vol.% Mo graded hollow cylinder.

particles may be adhered to Mo and there may be homogeneous adherence and/or coating of mullite on Mo powder during the ball mixing. Thus, composite powder taken as starting material decreased the Vickers hardness in mullite rich region. It is worth noting that FGM hollow cylinders fabricated by instant mixing of mullite and Mo powders had high hardness near to the pure mullite in the ceramic rich region. From Fig. 7, it can be seen that 40 vol.% Mo graded cylinder fabricated by instant mixing of starting materials without ball mixing had an increased hardness of around 12 GPa. The slight decrease in the Vickers hardness from the theoretical values can be explained due to the presence of porosities. Also, the hardness is almost equal in outer surface where the metal concentration is high and the gradient of Mo in metal rich region is small. The similar hardness values in the Mo rich region found in specimens of both type of mixing processes may be due to the interconnected structures of Mo grains.

4. Conclusions

Mullite–Mo graded hollow cylinders were successfully fabricated and developed by the centrifugal molding technique. Alcohol based slips were utilized with small concentrations (0.5 wt.%) of binder and dispersant. Faster drying rate was employed for graded cylinders in partial vacuum to avoid drying cracks. Thermo gravimetric analysis revealed that reduced atmosphere is ideal for sintering mullite–Mo FGM hollow cylinders. No additional phases were present when sintering was carried out at 1600 °C in H_2/N_2 atmosphere controlled furnace. SEM micrographs showed that there was a uniform gradient of Mo from mullite rich region towards outer direction. Graded specimens prepared from instant mixing of starting materials rather than mixing of pre-mixed composite powder had characteristic microstructures with isolated Mo grains in mullite rich region and uniform gradation of Mo was observed along radial direction. Interconnected Mo structures were present at the outer surface of hollow cylinder in which the hardness values became constant.

Acknowledgements

The authors would like to thank Professor Ohsato and Dr. Andrei of the Materials Science Department, Nagoya Institute of Technology, Japan for their support during the course of work.

References

1. Sarkar, P., Datta, S. and Nicholson, P. S., Electrophorectic forming of functionally graded materials. In *Functionally Graded Materials: Manufacture, Properties, and Applications, Ceramic Transactions*, ed. A. Ghosh, Y. Miyamoto, I. Reimanis and J. J. Lannutti. The American Ceramic Society, OH, USA, 1997, pp. 15–30.
2. Torrecillas, R., Espino, A. M., Bartolome, J. F. and Moya, J. S., Functionally graded zircon–molybdenum materials without residual stresses. *J. Am. Ceram. Soc.*, 2000, **83**(2), 454–456.
3. Takabe, H., Teshima, T., Nakashima, M. and Morinaga, K., Powder processing technique for development of zirconia–nickel functionally gradient materials. *J. Ceram. Soc. Jpn*, 1992, **100**(4), 387–391.
4. Yeo, J. G., Jung, Y. G. and Choi, S.-C., Zirconia-stainless steel functionally graded material by tape casting. *J. Eur. Ceram. Soc.*, 1998, **18**, 1281–1285.
5. Moya, J. S., Sanchez-Herencia, A. J., Requena, J. and Moreno, R., Functionally gradient ceramics by sequential slip casting. *Mater. Lett.*, 1992, **14**, 333–335.
6. Fukui, Y., Fundamental investigation of functionally gradient material manufacturing system under centrifugal force. *JSME Int. J. Series III*, 1991, **34**(1), 144–148.
7. Fukui, Y., Yamanaka, N. and Enokida, Y., Bending strength of an Al–Al_3Ni functionally graded material. *Composites Part B*, 1997, **28B**, 37–43.
8. Zhang, J., Wang, Y. Q., Zhou, B-L. and Wu, X.-Q., Functionally graded Al/Mg_2Si in-situ composites prepared by centrifugal casting. *J. Mater. Sci. Lett.*, 1998, **17**, 1677–1679.
9. Gao, J. W. and Wang, C. Y., Modelling the solidification of functionally graded materials by centrifugal casting. *Mater. Sci. Eng A*, 2000, **292**, 207–215.
10. Chu, J., Ishibashi, H., Hayashi, K., Takebe, H. and Morinaga, K., Slip casting of continuous functionally gradient material. *J. Ceram. Soc. Jpn.*, 1993, **101**(7), 818–820.
11. Requena, J., Morena, R. and Moya, J. S., Alumina and alumina/zirconia multilayer composites obtained by slip casting. *J. Am. Ceram. Soc.*, 1989, **72**(8), 1511–1513.
12. Tuffe, S. and Marple, B. R., Graded casting: process control for producing tailored profiles. *J. Am. Ceram. Soc.*, 1995, **78**(12), 3297–3303.
13. Sotirchos, S. V., Scale up issues in the preparation of functionally graded materials by chemical vapor deposition. In *Functionally Graded Materials: Manufacture, Properties, and Applications, Ceramic Transactions*, ed. A. Ghosh, Y. Miyamoto, I. Reimanis and J. J. Lannutti. The American Ceramic Society, OH, USA, 1997, pp. 31–46.

14. Khor, K. A. and Gu, Y. W., Effects of residual stress on the performance of plasma sprayed functionally graded ZrO_2/NiCoCrAlY coatings. *Mater. Sci. Eng. A*, 2000, **277**(1–2), 64–76.
15. Shinohara, Y., Imai, Y., Ikeno, S., Shiota, I. and Fukushima, T., Thermal stability of plasma-sprayed Ni–Cr–Al–Y/PSZ FGM in uniform and gradient temperature fields. In *Functionally Graded Materials, Ceramic Transactions*, ed. J. B. Holt, M. Koizumi, T. Hirai and Z. A. Munir. The American Ceramic Society, OH, USA, 1993, pp. 255–262.
16. Sarkar, P., Huang, X. and Nicholson, P. S., Zirconia/alumina functionally gradiented composites by electrophoretic deposition technique. *J. Am. Ceram. Soc.*, 1993, **76**(4), 1055–1056.
17. Zhao, C., Vandeperre, L., Vlengels, J. and Vander Biest, O., Cylindrical Al_2O_3/TZP functionally graded materials by EPD. *Br. Ceram. Trans.*, 2000, **59**(6), 284–287.
18. Sarkar, P., Datta, S. and Nicholson, P. S., Functionally graded ceramic/ceramic and metal/ceramic composites by electrophoretic deposition. *Composites B: Eng.*, 1997, **28**(1–2), 49–56.
19. Nishikawa, T., Masuda, A, Honda, S., and Awaji, H., Thermal shock resistance of alumina/nickel functional gradient material prepared by centrifugal casting. In *Functionally Graded Materials, Edited by International Liaison Forum of Functionally Graded Materials*. 1999, **13**, 107–113 (in Japanese).
20. Sivakumar, R., Nishikawa, T., Honda, S., Awaji, H., Fabrication and characterization of continuous graded stress-relief-type hollow cylinder FGMs. In *Proceedings of International Symposia on Materials Science for the 21st century ISMS-21*. Osaka, Japan, 2001, pp. 114–117.
21. Tomsia, A. P., Saiz, E., Ishibashi, H., Diaz, M., Requena, J. and Moya, J. S., Powder processing of mullite/Mo functionally graded materials. *J. Eur. Ceram. Soc.*, 1998, **18**, 1365–1371.
22. Sivakumar, R., Doni Jayaseelan, D., Nishikawa, T., Honda, S. and Awaji, H., Influence of MgO on microstructure and properties of mullite–Mo composites fabricated by pulse electric current sintering. *Ceram. Int.*, 2001, **27**, 537–541.
23. Diaz, M., Bartolome, J. F., Requena, J. and Moya, J. S., Wet processing of mullite/molybdenum composites. *J. Eur. Ceram. Soc.*, 2000, **20**(12), 1907–1914.
24. Kim, K.-H., Cho, S.-J., Kim, D.-H. and Yoon, K.-J., Centrifugal casting of large alumina tubes. *Am. Ceram. Soc. Bull.*, 2000, **79**(11), 54–56.
25. Sivakumar, R., Doni Jayaseelan, D., Nishikawa, T., Honda, S. and Awaji, H., Mullite–molybdenum composites prepared by pulse electric current sintering technique. *J. Eur. Ceram. Soc.* 2002, **22**(5), 761–768.
26. Ishibashi, H., Tobimatsu, H., Matsumoto, T., Hayashi, K., Tomsia, A. P. and Siaz, E., Characterization of Mo–SiO_2 functionally graded materials. *Metall. Mater. Trans. A*, 2000, **31A**, 299–307.
27. Awaji, H. and Sivakumar, R., Temperature and stress distributions in a hollow cylinder of functionally graded material: the case of temperature-independent material properties. *J. Am. Ceram. Soc.*, 2001, **84**(5), 1059–1065.