

Sintering and microstructure of mullite–Mo composites

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Abstract

Mullite–Mo composites of different compositions (0–100 vol.% Mo) were sintered to near theoretical density by pulse electric current sintering (PECS). The densification behaviour and the microstructure of mullite–Mo composites as a function of Mo content were studied. The addition of 10 vol.% Mo significantly enhanced the strength and toughness of monolithic mullite to 556 MPa and 2.9 MPa m^{1/2}, respectively. SEM observations revealed the modification of discrete isolated Mo particles to continuously interconnected network with the increase in the Mo content. Mo grains were located at the grain boundaries as well as inside the mullite grains. The addition of Mo to monolithic mullite led to a change in the fracture mode. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Several breakthroughs have been made in the past decade in high performance ceramics that possess properties capable of changing the traditional image of ceramic materials. The successful preparation of reliable ceramics, which possess high tolerance for catastrophic failure, may be one of the strongest impacts on the ceramic community. To tackle this setback, recent studies have been carried out with the aim of increasing ceramic toughness to produce ceramic composites by reinforcing metallic particulates, such as Ni, Cr, Mo, W, etc., which have innate properties such as plastic and electric conductivity. Though, a lot of research has been carried out in the ceramic/metal system by incorporating these transition metals with alumina and zirconia,^{1–7} when considering electrical conductivity, TEC mismatches, melting points and Young's modulus, the optimized choice of metallic phase for making structural ceramic composite is W or Mo.⁸

Although, many reports are available for Mo reinforced ceramic composites,^{9–11} composites of the mullite–Mo system have been studied a little. Furthermore, this system has the unique advantage of having similar thermal expansion coefficient values ($\alpha_{\text{Mull}} = 5.13 \times$

$10^{-6} \text{ } ^\circ\text{C}^{-1}$ at 1000 °C and $\alpha_{\text{Mo}} = 5.75 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ at 1000 °C). Thus, the residual stresses due to the thermal expansion mismatch are expected to be very small and hence, this class of system can be used as stress relief type ceramics. Hence, the densification behaviour of the mullite–Mo system and corresponding microstructure and properties are the subjects of interest of the present study. Recently, Bartolome et al.,⁹ fabricated mullite–Mo (32 vol.%) in vacuum and in reducing condition at 1650 °C. However, the densification behaviour of the entire range of composition (0–100 vol.% Mo) is not documented. In this context, recently we fabricated the mullite–Mo system of different compositions by pressureless sintering.¹¹ Although the condition was made in order to have a non-oxidizing atmosphere, control of oxidation of Mo grains was difficult during the addition of a higher amount of Mo, which in turn affected the mechanical properties of the composites. Therefore, mullite–Mo composites containing Mo above 30 vol.% could not be fabricated under normal atmosphere and pressure. As a continuation to that, fabrication of mullite–Mo composites of different compositions ranging from 0 to 100 vol.% Mo is the main subject of interest of this work. The pulse electric current sintering (PECS) technique,^{12–17} a kind of pressure assisted sintering, has been employed to sinter mullite–Mo composites, which is generally accepted to have control over the microstructural homogeneity and to improve the mechanical properties.

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Recently it has attracted increasing interest from many ceramists. To date, it has been accepted that grain growth can be suppressed during the PECS process because of very short sintering time, although a clear mechanism of sintering is in speculation.

2. Experimental procedure

Mullite (Kyoritsu Yowgow Co. –KM 102, d_{50} —1.3 μm) and Mo (Mitsuwa's Pure Chemical Co., d_{50} —2.7 μm) were used as the starting materials. 0.5 wt.% of SrO (Mitsuwa Spupe Chemicals.) was added as a sintering aid for mullite.¹⁸ All the powders were wet ball mixed in appropriate ratio in a polythene jar for nearly 24 h in ethanol medium using alumina balls as the grinding media. The milled slurry was dried in oven at 60 °C then dried at 110 °C for nearly 24 h and was screened through a No. 250 mesh sieve. The sieved powder was packed in a cylindrical graphite die with graphite punches on both sides and sintered by the PECS method (Model SPS-1050, Sumitomo Coal Mining Co., Ltd., Kanagawa, Japan) under an applied load of 15 MPa in vacuum. The inner wall of the graphite die was coated previously with BN to avoid any contact between the powder and the graphite die. The temperature was increased at a rate of 100 °C/min up to the sintering temperature. After holding for less than 5 min at the sintering temperature, the d.c. power was shut off to let the system rapidly cool at a rate of >300 °C/min. During sintering, the linear change in shrinkage was recorded by monitoring the displacement of the sample along the press direction. It should be noted that the temperature was measured with an optical pyrometer focusing on the surface of the graphite die but not directly on the specimen, and there probably existed a difference between the temperature of the die and the specimen considering faster heating rates and shorter holding times.

Relative density was determined by Archimedes method. The sintered specimens were cut and polished and the microstructure of the polished surface and the fractured surface was observed with a scanning electron microscope (SEM, Model–LEICA STEREOSCAN S440). Grain size was measured by linear intercept method. Hardness was measured by Vicker's indentation by applying a load of 10 kgf for 15 s. Fracture toughness was measured by both indentation fracture and SEVNB method. Bend strength was measured by 3-pt. Bending test for the samples with a span of 16 mm. Elastic modulus was determined by pulse echo method.

3. Results and discussion

Fig. 1 shows the relative density of the mullite–Mo (10 vol.%) composite as a function of sintering temperature.

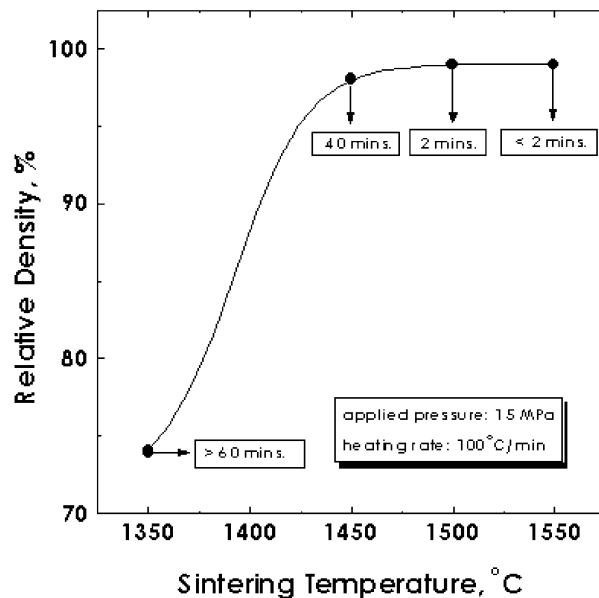


Fig. 1. Relative density of mullite–Mo (10 vol.%) composites as a function of sintering temperature.

It has been observed that the composite could not be densified completely at 1350 °C even after 1 h soaking and this shows the poor sinterability of the mullite matrix. The relative density increased with the sintering temperature, attained densification at 1450 °C, above which, it remained constant. At 1450 °C, however, it required nearly 40 min for the complete densification, whereas at 1500 °C, densification was complete within 2 min. Considering faster heating rate and shorter soaking time, sintering the composites at 1500 °C would be optimum for the improvement of the properties.

Fig. 2 shows the density measurements of the mullite–(0–100 vol.%) Mo composites sintered by the PECS

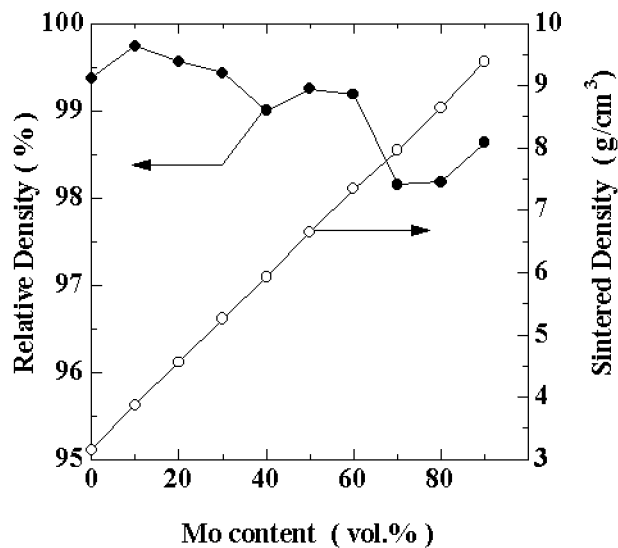


Fig. 2. Density measurements of mullite/(0–100 vol.%) Mo composites.

technique. A similar sintering condition has been used for all the compositions. It is observed from Fig. 1 that most of the samples have been sintered to nearly 99% of theoretical density within a few minutes, whereas densification of mullite–Mo composites by conventional sintering required more than 2 h.¹¹ Hence, sintering the composites by PECS would lead to constrained grain growth with a finer microstructure. It is observed that the density of the composites remained constant, i.e. ~99% of the theoretical value up to 60% Mo content and after that the relative density was reduced little. This sintering behaviour is closely related to the formation of large agglomerates at high Mo content during ball mixing and hence leads to the formation of closed pore in the composites containing higher volume content of Mo.

Fig. 3 shows the linear change in shrinkage of the specimens [mullite–Mo (0, 10, 20, 30 vol.%)] as a function of temperature during sintering. The plateau between 900 and 1150 °C corresponds to the rearrangement and initial necking of the particles through surface diffusion and hence involved no appreciable shrinkage.

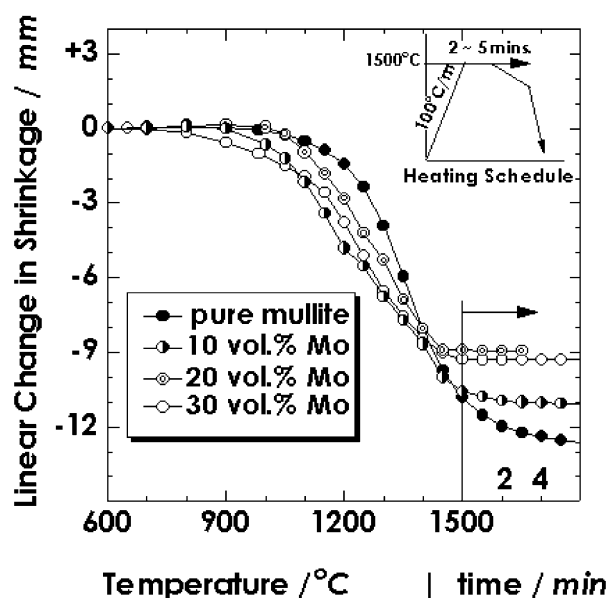


Fig. 3. Linear change in shrinkage of mullite–Mo composites during sintering.

But, it is noticeable that the whole shrinking process, from onset to end, took about only a few minutes. This indicates the tremendous driving force for diffusion, which facilitated enhanced sintering of mullite–Mo composites during the PECS process. It is also observed that the densification of monolithic mullite started at a slightly higher temperature, around 1100 °C, when compared with composites. Moreover, the composites attained densification within 2–3 min at 1500 °C, whereas the monolithic mullite required a little more time at the sintering temperature. This is attributed to the softening of Mo at higher temperatures. Hence, the elongated molybdenum particles formed due to high temperature plasticity coalesce together by necking, which enables faster densification of the metal (Mo) containing composites compared to monolithic mullite.

Table 1 summarizes the mechanical properties of mullite–Mo composites. In the case of pressureless sintering, the formation of pores due to the oxidation of Mo grains, and the excessive grain growth, deteriorate the mechanical properties of the composites. However, in the case of hot-press, the absence of MoO₂ in the mullite–Mo composites (i.e. as a consequence of its processing in reducing conditions) increases the strength of the metal-ceramic interface and the plasticity of the metal particles strengthening the material by a crack-bridging mechanism. However, it is observed that the composites sintered by PECS have better mechanical properties than the compacts sintered by hot-press and pressureless sintering. It is clear from Table 1 that very little addition of Mo (10 vol.%) has a significant effect on the mechanical properties of mullite, though it has little effect on fracture toughness. Although, there is only a small difference in the thermal expansion between mullite and Mo at room temperature, considering the thermal expansion, elastic modulus, Poisson's ratio and sintering temperature, it is expected to lead to potential stresses. The stresses would produce tension in the metal and compression in the ceramic, which could account for the increase in measured strength as Mo is added to mullite. Hence, the increase in strength could be related to a finer microstructure of mullite matrix and the residual stresses developed due to mismatch of thermal expansion at high temperatures

Table 1
Mechanical properties of mullite–mo composites

Vol.(%) Mo	σ_f (MPa)	K_{IC} MPa.m ^{0.5}	E GPa	H_v (GPa)	Sintering method ^a	Ref.
0	320 (15)	1.9 (0.2)	220 (7)	11.0	HP	9
32	530 (25)	6.7 (0.5)	242 (4)	7.3	HP	9
0	–	1.7 (0.4)	215 (5)	12.2	PLS	11
15	–	3.1 (0.5)	227 (5)	11.3	PLS	11
0	450 (50)	2.6 (0.4)	223 (3)	13.0	PECS	Present study
10	556 (40)	2.9 (0.4)	232 (3)	11.6	PECS	Present study

^a HP—hot pressing; PLS—pressureless sintering; PECS, pulse electric current sintering.

and elastic modulus between mullite and Mo. Although, crack deflection could be the plausible mechanism operating in the mullite–10 vol.% Mo composition, it is premature to generalize the toughening mechanisms in the mullite–Mo composites without any further detailed study.

Fig. 4 shows the microstructures of mullite–Mo composites sintered at 1500 °C by the PECS process. Fig. 4a shows the microstructure of the thermally etched mullite. Monolithic mullite exhibited duplex microstructure consisting of very fine equiaxed and elongated grains. There was no appreciable grain growth, when comparing the particle size of the starting material. Fig. 4b shows the microstructure of the mullite–20 vol.% Mo composite.

Mo grains were uniformly dispersed in the mullite matrix. However, in the case of pressureless sintering, inhomogeneity is a matter of agglomerate formation caused by non-uniformity in the packing.¹¹ This inhomogeneity can be prevented when sintering is accomplished by pressure, during the initial stage of sintering. In the low concentration range of Mo content, it was recognized that sub-micron sized Mo particles were dispersed at the grain boundaries of the fine-grained mullite grains. These fine Mo grains are likely engulfed in mullite grains as they grow. On the other hand, with increasing Mo content, up to 20 vol.%, slight grain growth of Mo particles was observed. In the range of 40 vol.% Mo, the formation of elongated Mo polycrystals,

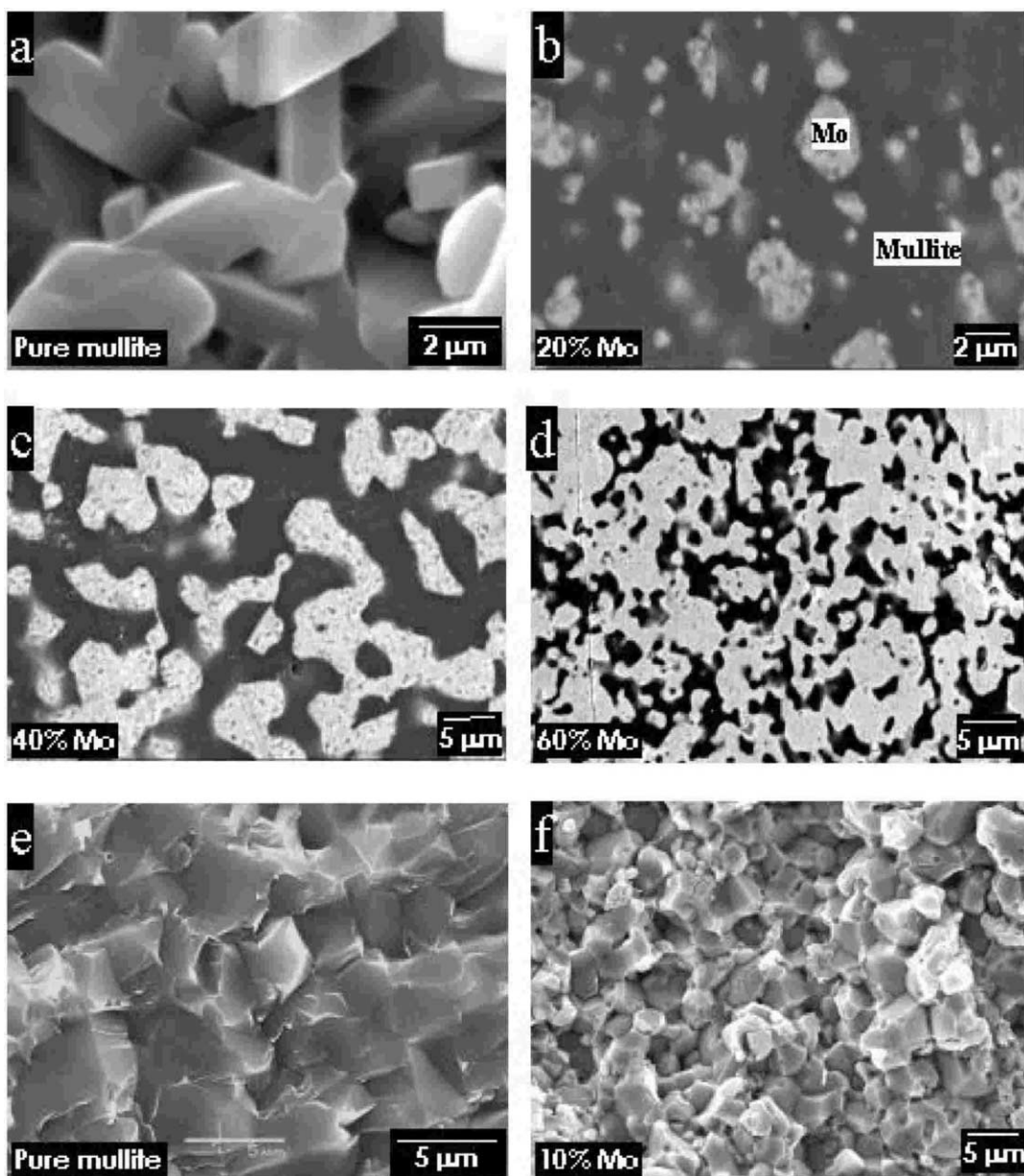


Fig. 4. Microstructures of mullite/Mo composites; (a) pure mullite (thermally etched at 1400 °C); (b) mullite/20 vol.% Mo; (c) mullite/40 vol.% Mo; (d) mullite/60 vol.% Mo, (e) fracture surface of pure mullite; (f) fracture surface of 10 vol.% Mo.

which were formed due to the necking of the Mo polycrystals, was observed. It is observed from Fig. 4d, that mullite–60 vol.%Mo composite had elongated Mo grains with an interconnected network. This kind of microstructural modification from discrete isolated metal particles to interconnected network is advantageous in improving the mechanical properties of the composites.

The fracture surface of the monolithic mullite (Fig. 4e) exhibited completely transgranular mode of fracture, indicating a strong grain bonding. Fracture surface of mullite–10% Mo composites, (Fig. 4e) reveals that Mo grains were located at both inter and/or intragranular position. The primary reason for the production of intragranular Mo is mainly induced by the grain growth of mullite in the sintering stage. The dragging force of these fine Mo is not strong enough to pin the grain boundary of mullite in position. As a result, the Mo is engulfed in the growing mullite. On the contrary, large Mo grains stayed at mullite grain boundaries throughout the entire sintering process, resulting in smaller mullite grains. As some of the grains were located at the grain boundary and mainly at triple junctions, the intergranular fracture mode was also observed. From these results, it can be seen that the microstructure of the composites can be designed by optimizing processing parameters, such as the content of Mo, sintering atmosphere, temperature, pressure and spatial arrangement of powder packing to fabricate Mo/metal ceramic nanocomposites.

4. Conclusion

Mullite–Mo composites with different compositions have been sintered at 1500 °C within a few minutes by the PECS method. All the composites have been sintered to 97–99% of the theoretical density. The instantaneous heat transfer and hence the mass transfer accomplished during pulse electric current sintering is the tremendous driving force for the densification of mullite–Mo composites. Mo grains tend to coalesce as soon as the mullite grains grow in the matrix occurring in the final stage of pressure assisted sintering and tend to form an interconnected network at higher vol.% of Mo containing composites. It is also being expected that considering the microstructure, coefficient of thermal expansion and the Poisson's ratio, toughening may occur by one or more of several mechanisms. The large modulus difference between Mo and mullite may result in the activation of a toughening mechanism not seen in other ceramic/metal system. The modulus difference between mullite and Mo is opposite that of many of the composite systems studies. Typically, the ceramic has the higher modulus, but in this case, Mo has the higher value. This opens the possibility of other crack deflection or energy absorption mechanisms and these discussions will be published in our next paper.

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