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Net shape ceramic microcomponents by modified sol–gel casting

C. M. Chan, G. Z. Cao, T. G. Stoebe

Abstract Development of ceramic microcomponents can open up the current silicon-based MEMS (micro-electro-mechanical systems) technology to new applications, especially for use in high temperature, chemically reactive environments. We report a study of sol–gel technologies applied to the fabrication of microcomponents. Organic/inorganic hybrid materials, particularly silica-based hybrids, were developed by sol–gel processing. A weak silica network was made possible by using acid catalyst, low functionality organic precursor in the sol preparation. Since the weak network has a high tendency to collapse, the result is a denser material. Incorporation of organic ligands modifies the surface chemistry of gel network so that a greater drying stress was developed and a denser hybrid structure was achieved without high temperature treatment. In addition, the incorporation of organic ligands prevented formation of cracks. Nanoscale oxide particles were dispersed and incorporated into the gel network by surface condensation. The incorporation of titania nanoparticles into sols greatly reduced the volume shrinkage of gels and enhanced the mechanical strength of the components. In this work, silica sol was also applied to coat metallic microcomponents and a thin uniform coating was formed.

1
Introduction

Ceramic materials present opportunities to widen the applications of microcomponents in micro-electro-mechanical systems (MEMS), due to their excellent chemical, thermal and abrasion resistance, in addition to their various unique physical properties such as electrical, optical and magnetic properties. However, the development of ceramic microcomponents is currently limited by the lack of suitable shaping techniques. Conventional shaping techniques such as injection molding are costly and require long-term equipment development. In addition, it is difficult to fabricate ceramic components with detailed micro-scale futures using the conventional molding techniques, since molding slurry typically consists of micrometer sized particles, solvent, dispersant and binders [Kingery et al. (1976), Rahama (1995)]. In spite of the above mentioned difficulties, Ritzhaupt-Kleissl et al. (1996) and Bauer et al. (1998) have made a significant progress in development of ceramic microcomponents by slip-casting.

Sol–gel casting or molding, however, is a simple, flexible and relatively inexpensive method for fabricating ceramic microcomponents, particularly for mass production, providing that precision micro-molds can be readily made. Deep X-Ray Lithography (DXRL) [Guckel (1993)] is a suitable technology that produces sub-micron tolerance, high-aspect ratio micro-molds in polymethylmethacrlate (PMMA) that can be utilized for this type of sol–gel casting purposes. Sol–gel technology offers several desirable processing advantages granting high quality microstructures: low processing temperature, atomic-level homogeneity for multi-component systems, simple processing procedures, low cost and environmental friendliness [Brinker and Scherer (1990), Pierre (1998)]. In addition, sol–gel processing is readily applicable to processing organic/inorganic hybrids and/or composites with tailorable composition and microstructure. Moreover, a variety of ceramic materials with properties such as ferroelectricity, piezoelctricity and magnetic property can also be made easily via sol–gel processing [Laubersheimer et al. (1998)]. Furthermore, sol–gel processing can be readily applied to introduce hydrophobicity or biocompatibility onto the surface of microcomponents. The reason that sol–gel processing is not commonly used in the production of ceramic monoliths is due to substantial shrinkage and subsequent cracking problems during drying due to high drying stress gradient; high porosity of the resultant gel structure is also problematic. In order to produce ceramic microcomponents using sol–gel processing, several technical challenges need to be overcome, which include avoidance of crack formation and reduction of volume shrinkage upon drying.

The strategies taken in this research to produce monolithic ceramic microstructures are development of organic/inorganic hybrid sol and incorporation of nanometer-sized ceramic particles into the hybrid sol–gel system. The incorporated organic components are anticipated to enhance the drying stress and reduce the gel

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network connectivity, so that a denser structure could be obtained upon removal of solvent; they are also expected to reduce crack formation by increasing the structural flexibility of the gel network [Judeinstein and Sanchez (1996)]. The nanometer-sized ceramic particles are anticipated to counteract the volume shrinkage and reduce the drying stress gradient, lowering the tendency of crack formation. In addition, the influences of mold materials on the ceramic microcomponent casting are discussed in detail.

2
Experimental

(a) Sol preparation

Polymeric hybrid silica sol was prepared by acid catalyzed hydrolysis and condensation of tetraethylorthosilicate, $Si(C_2H_5O)_4$ (TEOS, 98%, Aldrich) and 3-methacryloxypropyl-trimethoxysilane, $H_2C{=}C(CH_3)CO_2(CH_2)_3$-$Si(OCH_3)_3$ (MPS, 98%, Aldrich) in a mixture of ethanol, water and nitric acid (HNO_3) under vigorous stirring at 60 °C for 90 min to yield a stable sol that has a nominal molar ratio of TEOS:MPS:C_2H_5OH:H_2O:HNO_3 of $1{:}0.5{:}4.56{:}6.24{:}4.8 \times 10^{-3}$. The unhydrolyzable organic ligands, $H_2C{=}C(CH_3)CO_2(CH_2)_3$, linked to silicon with Si—C bonds were incorporated into silica network through co-polymerization.

(b) Incorporation of TiO_2 particles into hybrid organic silica sol

Nanometer-sized TiO_2 particles (~50 nm in diameter, Nanophase Tech. Corp.) were slowly added into the above prepared hybrid organic silica-sol in a molar ratio of 1:1 of TiO_2 to SiO_2 with vigorous stirring. The subsequent dispersion was ultrasonicated for 5 min and its pH value was adjusted to approximately 2 by adding an appropriate amount of nitric acid, so as to obtain a stable TiO_2 dispersed silica sol, which hereinafter is referred to as sol dispersion.

(c) Mold filling and separation

Figure 1 schematically illustrates the multi-step molding process of fabricating sol–gel ceramic microcomponents. The molds, utilized in this research, were fabricated by the standard DXRL [Guckel (1993)]. To improve the wettability of the sol dispersion and the adhesion of sol–gel derived microcomponents on the molds, the surface of the mold, of which the side-walls are PMMA and the bottom is Ni/Cu alloy, were oxygen plasma etched for 60 s, under an oxygen pressure of 100 mtorr. The mold was then put into a small petri dish. The sol dispersion, with the nanoparticles well dispersed, was poured into the petri dish to completely cover the mold. A piece of Parafilm was used to cover the petri dish so that the sol dispersion can be left to dry slowly, so as to prevent cracking, in the mold in ambient conditions for a week. The excess ceramic layer formed on top of the DXRL mold was carefully polished away prior to de-molding. Lastly, the PMMA molds were dissolved with dichloromethane, $C_2H_2Cl_2$, (99.5%, Alfa-AESAR) at room temperature, leaving the resultant sol–gel cast ceramic microcomponents intact.

(d) Sol–gel coatings on metallic microcomponents

Silica sol was prepared in a similar way as described in part (a); the molar ratio of TEOS:C_2H_5OH:H_2O:HNO_3 used was $1{:}3{:}4.2{:}3.2 \times 10^{-3}$. The metallic microcomponents were first dip-coated with surfactant (X-Triton, Dow Corning) that was diluted with ethanol with a volume ratio of 1:10. Next, the silica sol was diluted with ethanol in a volume ratio of 1:4. The diluted sol was then dip-coated onto electroplated metallic microcomponents with a withdrawal rate of 30 cm/min.

3
Results and discussion

Homogeneous dispersion and stabilization of nanometer sized titanium oxide particles in hybrid organic-silica sol was achieved through a combination of ultrasonication and electrostatic stabilization. Ultrasonication provided mechanical vibration that enhanced mixing of TiO_2 particles and hybrid-silica sol; it also physically broke apart the agglomerates of TiO_2 particles. Lowering the pH value electrostatically stabilized the suspension and promoted deflocculation of titania particles. Incorporation of the nanometer-sized TiO_2 particles compensated large volume shrinkage of silica gel during drying, which is typical for sol–gel monoliths. The reduction in volume shrinkage would subsequently lead to a decrease in formation of cracks. The TiO_2 nanometer-sized particles, upon dispersion in silica sol, were expected to form chemical bonds with the silica network through co-condensation at the particle surface as schematically depicted in Fig. 2. The

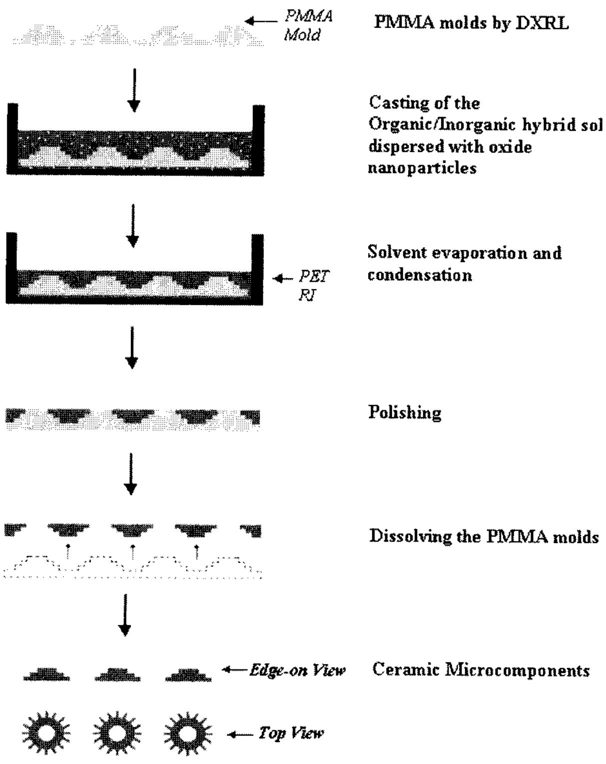

Fig. 1. Schematic illustration of multi-step modified sol–gel casting process for fabricating net shape ceramic microcomponents

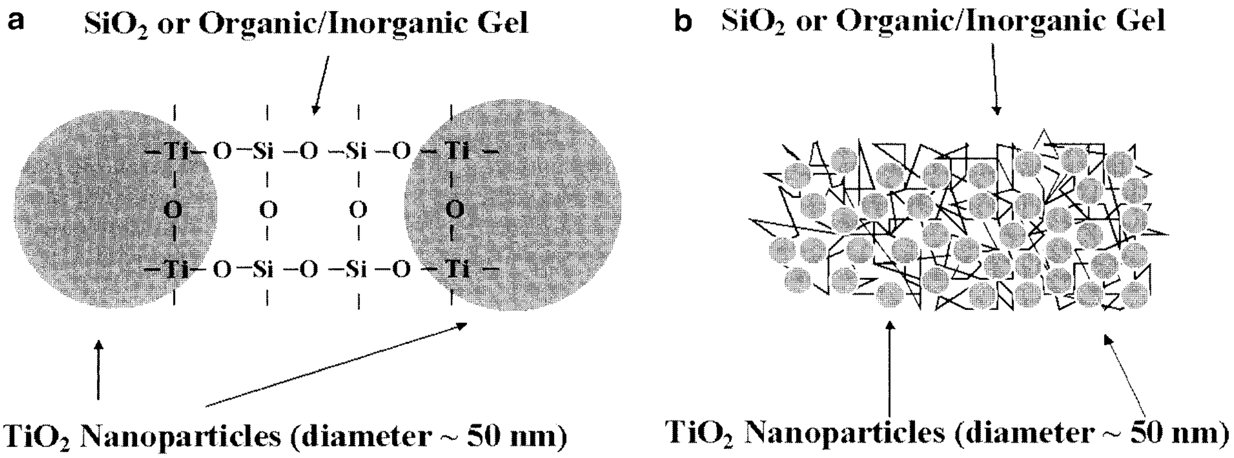

Fig. 2. Schematic illustration of TiO_2 nanometer-sized particles dispersed in sol–gel network and chemical bond formation with silica or organic components

formation of such chemical bonds between TiO_2 nanoparticles and silica gel matrix is desirable since such chemical bonds would significantly enhance the mechanical strength of the resultant ceramic microcomponents.

According to the literature, titanium alkoxide has a catalytic effect on silica sol [Brinker and Scherer (1990), Pierre (1998)]; introduction of titanium alkoxide would promote the hydrolysis and condensation processes of silica sol, resulting in a shorter gelation time and a significantly porous structure of the final xerogels [Chan et al. (1999)]. However, in the current research, we have not observed any appreciable influence of titanium oxide on gelation time and microstructure of the resultant ceramic composite, indicating that titania exerts no detectable influences on the sol–gel processing of silica systems.

Relatively dense ceramic microcomponents were obtained without subjecting to high-temperature heat-treatment, as usually required to obtain dense ceramics. The ambiently dried composite ceramic monoliths were ground up into powder and subjected to nitrogen sorption analysis at 77 K to determine the pore volume. The measured pore volume of the composite ceramics was very low, $\sim 2 \times 10^{-3}$ cm^3(STP)/g, meaning that the resultant ceramic microcomponents were relatively dense. The silica sol–gel system was chosen due to a number of advantages it offers. Silica has reasonably good mechanical properties including high hardness and wear resistance, thermal and chemical inertness. The polymeric nature of silica sol–gel allowed the formation of linear Si-O chains to be promoted during hydrolysis and condensation by using acid catalyst [Brinker and Scherer (1990), Pierre (1998)]. The formation of linear Si—O chains resulted in a weak gel structure that was readily to collapse during drying upon the removal of solvent and to form a dense xerogel without subjecting to heat treatment at elevated temperatures. Incorporation of unhydrolyzable organic ligands through co-polymerizing an additional sol-gel precursor, i.e. MPS, was another effort to maximize the capillary force within the sol-gel network and to reduce the connectivity of gel network via the low coordination number that MPS possesses (3 in MPS as compared to 4 in TEOS). Consequently, the weak network collapses more extensively into a denser structure [Cao et al. (1996)]. The incorporation of organic ligands also served another purpose, which was to enhance the plasticity of the gel structure, making it structurally more flexible and less prone to development of cracks during drying.

Mold filling, albeit seemingly a simple process, was a technical challenge for the reasons as follows: first, the mold must be filled completely with the dispersion, gas bubbles or voids are detrimental. Secondly, shrinkage of the dispersion upon evaporation of solvent is permitted only along the *Z*-direction, meaning that no shrinkage in the *X* and *Y* directions is allowed; this is extremely desirable since the microstructures have a high width to height ratio. To prevent lateral shrinkage, a good adhesion of sol dispersion onto the mold surfaces must be achieved. In the current research, partial chemical bonding was introduced into the interface between the sol dispersion and the mold. Prior to the mold filling, the surface of the molds was treated with an oxygen plasma etch, effectively altering the originally hydrophobic surface to hydrophilic, as indicated by the change of DI-H_2O advancing contact angle from >90° to <2°. Such hydrophilic surfaces resulted in perfect wetting and promoted complete filling of the sol dispersion into the molds. The oxygen plasma etch introduced hydroxyl groups [Egitto and Matienzo (1994), Gerenser (1993)] onto the surface of the PMMA side-walls, which then reacted with the silica sol-gel network to form C—O—Si bonds. Formation of such chemical bonds at the interface imparted superior adhesion between the gel network and the side-walls, thus effectively inhibiting unwanted lateral shrinkage of the gel during drying. This in turn led to the yielding of ceramic microcomponents that have net shape and detailed features as shown in Fig. 3. The optical microscopy image shown in Fig. 3a is a top view of the bottom surface of a composite ceramic microgear, the bottom surface is the surface facing the Ni/Cu of the mold before separation. The microgear was later mounted and the bottom surface was polished away. Shown in Fig. 3b is an image of one of the teeth of the microgear after polishing.

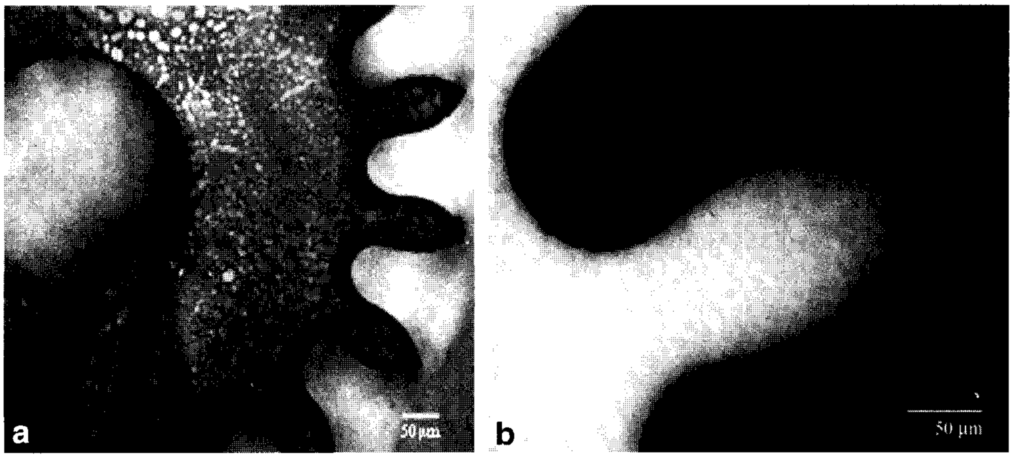

Fig. 3a, b. Optical microscopy images of sol–gel derived ceramic microgears, **a** a top view of the bottom surface and **b** an image of one of the teeth after the bottom layer was polished away

Figure 4 shows the SEM images of the bottom and the side-walls of the ceramic microgear made by modified sol–gel casting. The images reveal a highly porous bottom surface and dense, wrinkled side-walls. Such difference in surface microstructure can be explained as follows. In conventional slip casting, a casting mold, made of a porous material, provides capillary suction that removes the liquid and consolidates solid ceramic particles into a dense cast layer and the cast component then separates from the mold due to three-dimensional shrinkage [Reed (1988)]. In our case, the molds utilized consist of two types of materials: PMMA for the side-walls and Ni/Cu alloy for the bottom surface. The PMMA side-walls are partially permeable to the solvent which consists of water and ethanol, and thus allow the solvent in the dispersion to be removed due to the capillary force, similar to what happens in conventional casting. Consequently, condensation and solidification of sol dispersion occurs first at the PMMA surface. Conversely, the impermeable bottom metal surface of the mold does not provide the necessary capillary suction needed for solvent removal, the solvent in the dispersion could only be removed through the environment above the dispersion and the partial permeable PMMA side-walls. Therefore, solidification of the top surface of the sol dispersion and the surface adjacent to the PMMA side-walls occurs first and proceeds inwards since gelation begins near areas where solvent removal is allowed. In addition, since lateral shrinkage was inhibited due to the good adhesion between the PMMA side-walls of the mold and the cast microcomponents; the drying dispersion was only allowed to shrink in the *Z*-direction. Nonetheless, further shrinkage in the *Z*-direction would not assist in the densification of bottom layer of the cast parts. This is because the majority of the 'solid' material would first be consumed during the preceding shrinkage of the top surface of the dispersion where solvent removal is possible. In other words, by the time the bottom part of the casting begins to shrink, it is left with little 'solid' material for densification. The result is the formation of a porous layer at the bottom. A wrinkled side-wall shown in Fig. 4b is believed to be due to the progressive solidification from the top surface to the bottom.

There are several possible solutions to avoid the formation of hollow structure and/or wrinkled side-walls. One possible approach would be to reduce the drying speed, so that the condensation would occur more uniformly throughout the whole microcomponents and the material would have sufficient time to diffuse. The drawback, however, is that a slow condensation rate would result in a more porous (i.e., containing relatively large pores or a large number of pores) structure due to a reduced drying stress. The second possible approach would be to use step-wise molding procedure similar to the procedure applied by Lee et al. (1999). This approach will greatly minimize inhomogeneity in drying so that a more uniform structure would be obtained. However, this procedure is time-consuming and would only minimize the problem, not solving the problem completely. The third

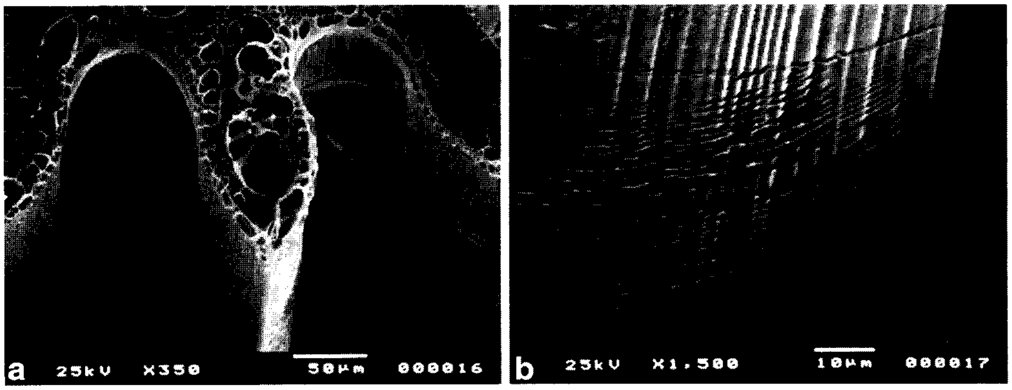

Fig. 4a, b. SEM images of **a** bottom surface and **b** side-walls of the ceramic microgear made by sol–gel casting

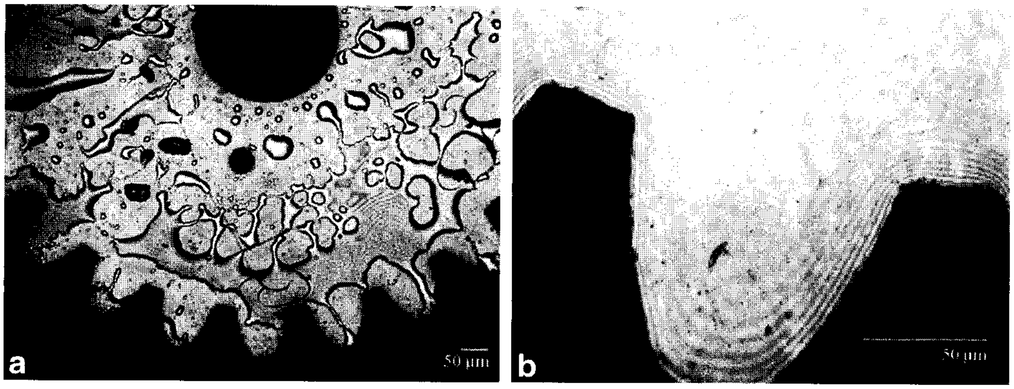

Fig. 5a, b. Optical microscopy images of diluted silica sol coatings on metallic microgears **a** without the use of surfactant, **b** with the use of surfactant

approach is to make casting molds using porous materials so that the solvent will be able to be sucked by the porous molds due to the capillary force. In this way, the condensation will occur first at the interface between the porous mold and sol–gel dispersion when the solvent is sucked into porous molds. The condensation proceeds inwards from the interface so that a solid structure would be formed. The fourth approach is to increase the amount of solid particles or the loading in the dispersion. The principle of the third and fourth approach is widely applied in slip casting, which is very well established as a shaping technique in the ceramic industry.

It is shown in Fig. 5, a uniform sol–gel silica coating on the metallic microcomponents. It was found that the initial deposition of surfactant onto the surface of metallic components prior to coating the components with silica sol was a crucial step to produce a uniform silica coating. Absence of the surfactant resulted in inability for the silica sol to evenly wet the surface of the metallic microcomponents. Nano-indentation analysis was performed on sol-gel silica coatings using a Hysitron Nano-Mechanical System attached to a Park CP scanning probe microscope (SPM) in the same manner as reported [11]. An average hardness value of $\sim$2 GPa was determined using a load of 300 N. In addition, ellipsometry analysis was performed on silica coatings on reference silicon substrates using a Rudolf Auto EL ellipsometer, the average measured thickness was found to be $\sim$90 nm.

4
Conclusions

A modified sol-gel casting technique was developed for fabrication of net shape ceramic microcomponents. The ceramic microgears made of sol-gel derived silica incorporated with organic components and TiO_2 nanometer-sized particles were fabricated. The sol dispersion completely wetted the surface and filled the molds granting subsequent net shape microgears with detailed features. It was found that the permeability and the surface properties of a mold were extremely important in the modified sol-gel casting. The ceramic microgears produced have dense side-walls due to partially permeable PMMA side-walls of the mold and the good wettability, but porous bottom surfaces owing to the impermeable bottom surface of the mold and restricted lateral shrinkage. In addition, sol–gel derived silica coatings were successfully deposited onto surfaces of metallic microcomponents which were first coated with surfactant. Further improvement of processing includes elimination of the porous bottom layer of the above-fabricated ceramic microcomponents, which could be achieved either by using solvent permeable molds or by multiple deposition via sol–gel casting.

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