Superparamagnetic Si$_3$N$_4$-Fe-Containing Ceramics Prepared from a Polymer-metal Complex

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Abstract: Functional non-oxide ceramics derived from liquid ceramic precursors with transition metal compounds have been studied for use under mechanically harsh conditions and high temperatures. Although the synthetic routes toward functional ceramics are challenging because of the reactivity and chemical properties of the elements, we introduced a simple route to fabricate magnetic non-oxide ceramics from commercially available sources. After dissolving ferric chloride in THF, the polyvinylilazane (PVS) was added to the solution. The molecular weight started increasing within a few minutes at room temperature, and the color became dark yellow. Particles of the mixed compound were obtained through evaporation of the THF. Curing at 130 °C was then undertaken, and the cured compound was pyrolyzed in the 500 ∼ 1000 °C temperature range under a nitrogen atmosphere. The obtained ceramics were analyzed using XRD, FT-IR spectroscopy, TGA, and TEM.

Keywords: ceramic, superparamagnetic, FeCl$_3$, ferromagnetic

Introduction

The development of microelectromechanical systems (MEMS) is a rapidly growing technology with a broad range of commercial applications for a diverse collection of evolving MEMS sensors for actuators. However, silicon and organic polymers, which are the most commonly employed materials for MEMS, cannot be utilized as structural materials under harsh conditions [1,2]. Therefore, there has been a major push to develop new fabrication techniques for tribological non-oxide ceramic MEMS that can survive at high temperatures and under corrosive conditions. The polymeric route to nonoxide ceramics provides a unique opportunity for manufacturing MEMS devices or their components through liquid fabrication and subsequent pyrolysis. Recently, Raj and coworkers demonstrated the fabrication of a SiC-based ceramic actuator and a combustion chamber on the millimeter scale using direct UV-photolithography of polymeric precursors [3].

Moreover, the development of functional polymer precursors is demandeds for the design or improvement of the unique performance of MEMS in microsystem technology [4,5]. In this context, polymeric routes toward the preparation of metal-containing ceramics have attracted more attention because the metal-containing polymeric precursors have versatile processibility and because the electrical and magnetic functions of the final ceramic products are readily tailored. Improved approaches with higher-precision formability are being demanded for newly emerging applications for electrically conductive components or small precision parts having complex geometries, e.g., microelectrodes, micro-sensors, and electric or magnetic devices. In contrast, conventional powder processing technologies are commonly used to produce the large particles with simple design.

Manners and coworkers reported the new magnetic application of preceramic polymers containing ferrocenophane [6]. Ozin with coworkers prepared a porous SiC ceramic with iron nanoparticles embedded after pyrolyzing a crosslinked polyferrocenylsilane [7]. Tsirlin group reported the synthesis of polycarbosilanes containing Zr, Ti, and Fe and alloys such as Mn-Rh, Ag-Co, and Cu-Ag for structural ceramic applications [8]. The Loye group prepared Mn-Rh, Ag-Co, and Cu-Ag mixed-metal coordination polymers that displayed enhanced electrical...
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Scheme 1.

conductivity and/or unique magnetic behavior [9]. In addition, we reported that Mo-containing polymethylsilane could be converted into an electrically resistant SiC-MoS2 ceramic [10]. These materials are very promising for use in MEMS such as microactuators, micromotors, and fluid micropumps [1,2,11,12].

In this paper, we report a simple procedure for the preparation of a magnetic phase-embedded SiC-based ceramic, SiCN/Fe, using a mixture of polyvinylsilazane (PVS) as a SiCN ceramic precursor and FeCl3. PVS is an inexpensive cyclic compound that reacts with FeCl3 in tetrahydrofuran (THF) in the absence of any catalyst. The properties and morphologies of the ceramic products obtained at different pyrolytic temperatures under a nitrogen atmosphere were also investigated.

**Experimental**

**Materials**

The PVS (Kion VL 20, www.kioncorp.com) used as a SiCN ceramic precursor was purchased from the Kion Corporation. Anhydrous THF, n-hexane, ethylene glycol dimethyl ether, and iron chloride were obtained from Aldrich and used without further purification. All reactions and manipulations were performed under purified nitrogen in a glove box. Glassware was either flame-dried or oven-dried.

**Synthesis of Oligomers for SiCN/Fe**

When 0.1, 0.2, and 0.3 g of FeCl3 were dissolved in 2, 4, and 6 g of THF, respectively, with gently stirring for 15 min, the mixtures became pale-green with a slight amount of heat generated from the exothermic reaction. After complete dissolution of FeCl3, 1 g of PVS was added to each of the mixtures, designated as PVS-1, PVS-2, and PVS-3, respectively. The mixtures quickly turned to black solutions with exothermic heat, and gradually formed yellow gels upon standing under a dry nitrogen atmosphere for several hours. Black solids finally precipitated, leaving supernatant pale yellow liquids, when left standing for a day, followed by centrifugal separation. In addition, the supernatant was dried to recover the remaining solid product.

**Curing and Pyrolysis**

The separated solid products were cured at a temperature of 130 °C for 24 hr under vacuum and then they were placed in an alumina ceramic boat and pyrolyzed in a quartz tube at 500~1000 °C under a nitrogen atmosphere at a heating rate of 10 °C/min to convert the polymer to magnetic ceramic products.

**Measurements**

Infrared spectra were obtained using a Genesis II FT-IR spectrometer. Powder X-ray diffraction (PXRD) data were obtained on a D/MAX-2200 Ultima/PC using Ni-filtered Cu Kα radiation (λ = 1.54056). Transmission electron micrographs (TEM) were recorded using a Leo EM912 Omega instrument. The thermal properties of the ceramics were studied through thermal gravimetric analysis (TGA, TA Instrument 2950) and the magnetic properties were recorded using a Vibrating sample magnetometer (VSM, LDJ 9600).

**Results and Discussion**

PVS is a versatile liquid thermosetting resin composed of silazane repeat units in which silicon and nitrogen atoms are bonded in an alternating sequence (Scheme 1).

The precursors of Si-C-N-M ceramics (M = metal) have been prepared through the condensation of silazane lithium or sodium salts with MCln (M = Fe, Ti, Zr; n = 2~4) [13]. However, in this study, PVS was directly reacted with FeCl3, without any pretreatment, in THF, as shown in Scheme 1. In particular, during the direct synthesis of the PVS-iron complex, we ascertained
that the metal complex was generated in situ from the Lewis acid-base reaction of THF and FeCl₃. To understand the mechanism of the formation of the PVS-iron complex, a series of reaction samples was analyzed using FT-IR spectroscopy. It is clear that the absorption bands attributed to the vinyl groups in the starting PVS polymer (C–Hvinyl at 3048 and 3007 cm⁻¹; C=C at 1593 cm⁻¹) did not change their appearance during the reaction. In contrast, the intensity of the Si–H (2129 cm⁻¹) and Si–N absorbance bands (1170 cm⁻¹) weakened continuously, and the N–H absorbance band at 3380 cm⁻¹ shifted and decreased in intensity [14]. From these spectral changes, we conclude that the vinyl groups were not involved in the reaction, but Si–N bonds were broken as the ring strain in the cyclic PVS might cause a ring opening reaction with FeCl₃. We believe that the polymer-metal complex that precipitated resulted from the reactions between N–H groups and FeCl₃ (as a Lewis acid-base reaction) and between Si–H groups and FeCl₃ (as substitution reaction) to form Si–N–Fe and Si–Fe–N bonds, respectively [13,15]. No differences resulting from changing the mixed ratios appeared in the FT-IR spectra.

The mass conversion of the polymeric complex to ceramic material, as measured by thermal gravimetric analysis (TGA) in Figure 2, was ca. 80 % in a nitrogen atmosphere at temperatures over 800 °C. It is a comparatively higher ceramic yield than that of 75 % for the PVS feedstock polymer, which is favorable for fabricating dense ceramic devices [16].

Figure 3 shows XRD patterns of the PVS-metal complex products pyrolyzed at various temperatures in a nitrogen atmosphere. The crystalline Fe particles began to be observed when annealed at 500 °C. Other crystalline matrix phases, assigned to NH₄Cl and Fe₃C, were also formed as the polymer-metal complex decomposed. When the samples were annealed at higher temperatures, it is interesting that various phase changes were observed. The formation of large α-Fe particles has been attributed to enhanced α-Fe mobility in the matrix at temperatures of 500 °C or above; bond cleavage in PVS readily occurs, facilitating matrix arrangement and Fe mobility [6]. The intensity of the NH₄Cl phase gradually decreased through thermal decomposition; it disappeared completely at 800 °C. However, the α-Fe crystalline phase survived persistently and coexisted with the Fe₃Si phase only at 800 °C. When the samples were heated above 800 °C, the atoms in the complex rearranged to form a crystalline Si₃N₄ phase with a highly intense α-Fe peak. It is surprising that the crystallinity of the Si₃N₄ phase developed fully at such a low temperature as 900 °C because a similar extent of crystallization was observed at over 1400 °C for the pure PVS-derived ceramic, as shown in Figure 3 [17]. However, it has been observed previously that even a slight presence of various metals enhances the crystallization of polymer-derived ceramic phases [18].
Alternatively, it is interesting to investigate the pyrolyzed products of the solids obtained from supernatant polymer-metal solutions PVS-1, PVS-2, and PVS-3 after vacuum drying. Figure 4 displays XRD patterns of the obtained ceramics pyrolyzed at 1000 °C. The ceramic products from PVS-2 and PVS-3 obviously showed the crystalline diffraction patterns corresponding to Si₃N₄ and Fe₃Si phases, indicating that the excess Fe species must form a soluble type of polymer complex with a smaller Fe loading content than the precipitated products. As expected, the pyrolyzed product from the PVS-1 sample with the lowest FeCl₃ ratio revealed no Fe-related peaks, only an amorphous phase in the 20 ~ 40 degree range. This observation provides additional evidence that the Fe species reacted preferentially with the silazane parts of PVS through intramolecular and intermolecular routes to form both types of precipitated and soluble complex products.

In addition, we observed (by TEM) that the metallic phase was embedded in the ceramic matrix. For the products heated at 500 °C, α-Fe grains (7 ~ 10 nm in size) remained in the amorphous matrix, whereas at 800 °C, the α-Fe grains were formed at ca. 15 nm in size. In particular, there was no crystalline growth after pyrolysis at higher temperatures. And it is concerned with super-paramagnetic property at 1000 °C [19].

Figure 5a displays a low-magnification TEM image showing independent Fe particles. However, the Fe₃C particles were able to interact with the matrix between the Fe particles, as observed in Figure 5d (high-magnification image). At 800 °C there is Si to the matrix of surroundings and confirmation it could not the Fe₃Si in TEM analysis. At 800 °C analyses put a trust consequently in XRD data.

A sample pyrolyzed at 1000 °C showed independent Fe particles in the low- and high-magnification images (Figures 5c and 5e, respectively). These TEM observations are in good agreement with the XRD results.

Figure 6 shows the magnetic properties of the ceramic products prepared at different pyrolytic temperatures; we were interested in correlating the magnetic properties of the materials with the pyrolytic temperatures. Samples prepared at 500, 700, 800, and 1000 °C were analyzed using a vibrating sample magnetometer (VSM). The magnetic behavior of the α-Fe particles prepared below 800 °C can be compared with that of α-Fe particles prepared at 1000 °C. The ceramic phase prepared at 500 °C showed soft ferromagnetic behavior. It possesses a saturation magnetization (Ms) of 27 emu/g and a coercive field (Hc) of 100 Oe. A sample pyrolyzed at 500 °C displayed room-temperature hysteresis and a small remnant magnetization (5 emu/g) consistent with a soft ferromagnet. On the other hand, the saturation magnetizations of the samples prepared at different temperatures were 30 (700 °C) and 25 emu/g (800 °C). A sample pyrolyzed at 800 °C exhibited the lowest magnetic properties because of the formation of Fe₃Si and the onset of rearrangement. At 1000 °C, there was a saturation magnetization of 50 emu/g. These samples showed no hysteresis at 1000 °C, and their magnetic saturations were gradual, consistent with the behavior of super-paramagnetic particles. The VSM measurements
thus demonstrated a transition from soft ferromagnetic $\alpha$-Fe particles to superparamagnetic $\alpha$-Fe particles at 800 °C [19]. Therefore, by varying the pyrolysis temperature, the $\alpha$-Fe particle size and magnetic properties of the resulting ceramics can be tuned [6].

**Conclusions**

We have discovered a simple route for fabricating magnetic non-oxide ceramics from commercially available sources. PVS reacts with FeCl$_3$ in THF in the absence of a catalyst. Cross-linking at 130 °C confirmed the occurrence of Lewis acid-base and substitution reactions. Varying the pyrolysis temperature permitted a study of the magnetic and crystalline properties. Magnetization data showed that the smaller $\alpha$-Fe particles in ceramics prepared at 500 °C exhibited ferromagnetic behavior, whereas the larger particles in materials prepared at 1000 °C displayed superparamagnetic behavior. The results obtained were consistent with the XRD data of Figure 3. This flexibility may be advantageous for particular materials applications.

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