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The preparation and characterization of polymer-derived Fe/Si/C magnetoceramics

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Abstract

In this work, the preparation of polymer-derived Fe/Si/C ceramics was achieved by synthesis and pyrolysis of the preceramic hyperbranched polyferrocenylsilane. The Fe/Si/C ceramics obtained under various experimental conditions such as different pyrolytic temperatures, atmospheres and heating rates, were investigated by TG-MS, XRD, and XPS. Moreover, the magnetic properties of the ceramics were investigated by the vibrating sample magnetometer (VSM). Experimental results indicated that the pyrolysis of the preceramic polymer started above 250 °C and completed among 800–1000 °C. The crystallinization of the pyrolytic product started at 500 °C. Besides the heat treatment temperature, the atmosphere and heating rate also played important roles in the composition and magnetic properties of the corresponding Fe/Si/C ceramics. Fe existed as α-Fe in ceramics sintered at 900 °C under N2 and NH3 atmospheres. However, the main components in ceramic product sintered under air were γ-Fe2O3 and carbon. Although all of the three ceramic products sintered under different atmosphere


were ferromagnetic with low remanent magnetization and coercivity, the ceramics sintered under NH$_3$ had the largest saturation magnetization. The saturation magnetization of the Fe/Si/C ceramics further ascended when fabricated under NH$_3$ with a slower heating rate, in which Fe existed as $\alpha$-Fe, Fe$_3$O$_4$ and $\gamma'$-Fe$_4$N.

**Keywords:** Fe/Si/C, ceramics, magnetic, precursor, polymer-derived

1 Introduction

Due to the high mechanical strength, good oxidation resistance at high temperatures, excellent abrasion resistance and supreme resistance to chemical corrosion, SiC ceramics have been extensively investigated in a variety of fields such as aviation industry, aerospace, weapons, etc.[1-5] By the incorporation of Fe, not only may the heat resistance and oxidation resistance of SiC be improve efficiently, but also the ceramics can perform magnetic, electrical and catalytic properties.[6-8]

The strategies to prepare Fe/Si/C ceramics by polymer-derived method could be concluded as follows: (1) Pyrolysis of the mixture of elemental metals or metal oxides with polymer precursors. Saha et al.[9] synthesized polymer precursor by crosslinking polysilazane (Ceraset) with Fe$_3$O$_4$ at 400 °C under N$_2$. Fe$_3$O$_4$ was reduced to $\alpha$-Fe at 700 °C during the pyrolysis process. The final ceramics sintered at 1000 °C had a high density of 4.8 gm/cm$^3$, high hardness (Hv=6.5 GPa) and magnetic properties. Yu et al. [10] reported that magnetic Fe/Si/C ceramics were prepared by the reverse microemulsion technique using Fe(NO$_3$)$_3$ and polycarbosilane (PCS). Fe distributed among the $\beta$-SiC phase in the Si/Fe/C ceramics sintered at 1200 °C in the form of Fe$_3$Si, with an average particle size of about 12 nm. Therefore, this strategy is the way to prepare ceramics that powders of metal or metal oxide are mixed uniformly with preceramic polymer, prior to crosslinking and pyrolysis of the mixture at high
temperature. Although the composition of the obtained ceramics can be effectively adjusted by adding different metal compounds and controlling the addition amounts, the final sizes of the metal particles in the ceramics are quite limited to their original sizes. Moreover, the metal content and their dispersity in the sintered ceramics cannot be regulated effectively. (2) Post-modification of polymer using Fe-containing compounds prior to pyrolysis[11-13]. Chen’s work[14] produced high-molecular-weight polycarbosilane containing Fe (named as Fe-PCS), by using low-molecular-weight polycarbosilane containing Fe (named as Fe-PCS), by using low-molecular-weight PCS and Fe(CO)₅. Subsequently, silicon carbide fibers were prepared using the Fe-PCS precursor, inside which Fe uniformly distributed as α-Fe domains. In 2014, AHPCS precursor polymer was chemically modified with vinyl ferrocene by Yu’s group[15] to obtain a modified AHPCS precursor. The Fe/Si/C ceramic was finally obtained by the pyrolysis of the precursor, resulting in a high ceramic yield of ~80% at 1200 °C under argon. Although it is a convenient way to introduce Fe to SiC ceramics through this strategy, the composition and structure of the post-modified preceramic polymers could not be well controlled, which is detrimental to the processability of the precursors in the preparation of ceramic products. (3) Direct pyrolysis of organometallic precursor polymers. Polyferrocenylsilanes (PFS), a series of organometallic polymers, attract increasing attention to be used as precursors for the preparation of Fe/Si/C ceramics[16-22] Peterson et al.[23] synthesized a series of linear PFS polymers by changing the substituent of Si atoms, which effectively improved the ceramic yield of linear PFS. Ginzburg et al.[24] reported that a crosslinked polyferrocenylsilane was prepared by the ring-opening polymerization of a spirocyclic ferrocenophane monomer. Furthermore, the composition of the ceramics obtained by pyrolysis of the precursor was altered as the pyrolytic atmosphere varied, which yielded SiC/C/Si₃N₄ ceramics containing α-Fe under N₂ and ceramics containing Fe₃Si₃ under Ar. This strategy has
obvious advantages over aforementioned two ones. The composition and property of the obtained ceramics can be effectively adjusted through the synthesis and pyrolysis of the preceramic organometallic polymers. Elements in the final ceramics can disperse uniformly, the crystalline size of which can be controlled by changing sintering conditions. It is readily to prepare Fe/Si/C ceramics of various shapes as the preceramic organometallic polymers usually have suitable processabilities.

In this work, Fe/Si/C ceramics were made from the hyperbranched polyferrocenylsilane as the preceramic organometallic polymers through the polymer-derived method. As mentioned above, the compositions and properties of the Fe/Si/C ceramic products are dependent greatly on the experimental conditions. Therefore, the polymer-to-ceramic pyrolytic transformation of the preceramic polymer was investigated in detail. The influences of experimental conditions such as sintering temperature, atmosphere and heating rate on the compositions, structures and properties of the obtained Fe/Si/C ceramics were explored. To the best of our knowledge, the preparation of Fe/Si/C ceramics from hyperbranched polyferrocenylsilane has not been systematically investigated with respect to the sintering temperature, atmosphere and heating rate.

2. Experimental

2.1. Materials

\(N\)-butyl lithium (\(n\)-BuLi, 2.4M in hexanes), tetramethylethylenediamine (TMEDA), trichloromethylsilane and benzophenone were purchased from J&K Technology Co., Ltd. All reactions unless otherwise noted were carried out under an atmosphere of dry nitrogen. Hexane and THF in the experiment were carried out with an anhydrous and anaerobic treatment prior to use. All other reagents and solvents were obtained at the highest purity and used without further purification unless stated.
2.2. Measurements

All reactions were carried out using standard Schlenk techniques under an inert atmosphere of oxygen-free nitrogen, unless otherwise stated. Fourier transform infrared spectroscopy (Spectrum Frontier FT-IR, Perkin Elmer, USA) was used in this study to analyze chemical structures of polymers between 400 and 4000 cm\(^{-1}\). \(^1\)H-NMR spectrum was recorded by NMR measurements (400/54/ASP, Agilent Technologies, USA) under 400 MHz. Molecular weights and molecular weight distributions of polymers were analyzed by a Wyatt gel permeation chromatography equipped with a Dawn Heleos-II detector, using THF as the eluent at a flow speed of 1 mL/min and sample concentration of 1 mg/mL. Polystyrene was applied as standard sample to calibrate the measurements. Thermal gravity analysis of polymers was obtained on the instrument of Pris 1 TGA, Perkin Elmer, USA, with a heating rate of 10 °C/min, a maximum temperature of 1000 °C under nitrogen atmosphere, and a gas flow speed of 50 mL/min. The XRD patterns were obtained by X-ray diffraction measurement (D8 Advance, Bruker AXS, Germany), using Cu target (\(\lambda = 0.154 \text{ nm}\)), measurement range 2\(\theta\) from 10 to 90° and a tube voltage of 40 kV. The X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific Escalab 250Xi machine with monochromatized Al anode X-ray source. Magnetic properties of ceramic powder were investigated by a vibrating sample magnetometer (VSM) with magnetic field range of 2 T at 300 K.

2.3. Synthesis of ferrocenyl dilithium [25,26]

10 g (53.8 mmol) of ferrocene and 70 mL of anhydrous hexane were added into a dry Schlenk flask and then stirred into suspension. 10 mL of TMEDA (66.7 mmol) was added, followed by adding dropwise 53 mL (127.2 mmol) of the solution of \(n\)-butyllithium in \(n\)-hexane (2.4M). The reaction was stirred overnight and then filtered.
under vacuum. The filtrate was removed and the residue was washed with anhydrous hexane for 3 times. Subsequently, hexane was removed by vacuum filtration at room temperature. 13.3g of ferrocenyl dilithium was obtained as orange red solid. The product was stored under Ar atmosphere prior to use.

2.4. Preparation of hyperbranched polyferrocenylsilane

5 g (18.2 mmol) of ferrocenyl dilithium was put into a dry Schlenk flask inside a glove box. The flask was then removed and put into a constant temperature bath (T=20 ℃). Subsequently, 50 mL of anhydrous THF was injected into the flask via a syringe. 30 mL of THF solution of 2.1 g (14.1 mmol) of Cl₃SiMe was added into the Schlenk flask dropwise through a pressure-equalizing dropping funnel. The reaction was stirred overnight, followed by the addition of 1 mL of MeOH into the solution to terminate the reaction. The resulting solution was then filtered, and the filtrate was concentrated and precipitated in methanol. Finally 2.1 g of hyperbranched polyferrocenylsilane as golden solid was obtained under vacuum desiccation.

2.5. Preparation of Fe/Si/C ceramics

The preparation of Fe/Si/C ceramics by pyrolysis of the hyperbranched polyferrocenylsilane precursor under N₂ and NH₃ was carried out in a quartz tube furnace, while that under air was finished in a muffle furnace. The typical process of the preparation was as follows. 1 g of polymer were placed in a ceramic crucible under nitrogen atmosphere, which was then transferred to a quartz tube furnace for pyrolytic experiments. Sample was heated from room temperature to the target temperature at a speed of 3°C/min and kept at the temperature for 2 h. The sample was then cooled spontaneously to room temperature. The obtained ceramics were collected for characterization.

3. Results and discussion
3.1. Preparation of preceramic organometallic polymers

As can be seen in Scheme 1, the synthetic route of hyperbranched precursor, ferrocene reacted with \( n \)-butyllithium as well as TMEDA in hexane solvent to synthesize ferrocenyl dilithium, which further reacted with methyltrichlorosilane to prepare the hyperbranched polyferrocenylsilane.

\(^1\text{H-NMR}\) spectrum of the hyperbranched polymer in CDCl\(_3\) is displayed in Fig. 1 (a). The peak at 7.2 ppm was the vibration peak of CDCl\(_3\) solvent. The broad peaks at chemical shift of 3.8~4.8 ppm belonged to hydrogen of ferrocenyl (Fc) groups, while the broad peaks at 0.75~1.5 ppm were attributed to the Si-CH\(_3\) units. The FT-IR spectrum of the polymer is shown in Fig. 1 (b). Peaks at 1633 cm\(^{-1}\), 1420 cm\(^{-1}\), 1160 cm\(^{-1}\), 1031 cm\(^{-1}\) and 830 cm\(^{-1}\) were from the characteristic vibration of Fc units, while the peak at 3080 cm\(^{-1}\) was from the vibration of the unsaturated C-H of the Fc units. The peak at 2960 cm\(^{-1}\) was derived from the asymmetric vibration of C-H in methyl groups, and peaks at 1252 cm\(^{-1}\) and 776 cm\(^{-1}\) from Si-CH\(_3\). Obviously, there existed a peak at 2170 cm\(^{-1}\), the vibrational peak of Si-Cl bonds, which were caused by the slightly excess addition of Cl\(_3\)SiMe to the reaction mixture.

The number average molecular weight \( M_n \) and weight average molecular weight \( M_w \) were determined by gel permeation chromatography (GPC), as shown in Fig. 2 (a). The \( M_n \) and \( M_w \) of the hyperbranched polyferrocenylsilane was 2.4×10\(^3\) and 1.2×10\(^4\), respectively, while the polydispersity index PDi was 4.9. The thermal behavior of the precursor during the pyrolysis is demonstrated by the TG curve (Fig. 2 (b)). It is evident from the TG curve that the precursor decreased quite slightly in weight below 250 °C, which underwent a drastic decrement in weight from 250 °C to 600 °C. After a gradual decline in weight between 600 °C and 800 °C, the sample eventually remained a stable
weight above 800 °C, ending with a ceramic yield of 40.8% at 1000 °C under an atmosphere of nitrogen.

3.2. The influence of pyrolytic temperature

During the pyrolytic process with increment of the temperature, preceramic polymer will experience a transformation from organic state to inorganic state. With the breakage of chemical bonds, as well as rearrangement and condensation of polymeric backbones, significant weight loss can be witnessed for the volatilization of small molecules. Pyrolytic temperature exerts a considerable influence on the composition, structure and properties of the obtained ceramics, hence study of the evolution of the precursor with increase of heating temperature is essential. The TG-MS spectra of the preceramic polymer are presented in Fig.3. The changes of the precursor as the temperature increased could be divided into the following three stages.

Stage 1: Before the pyrolysis (35~250 °C, weight loss of 5.0%). In this temperature range, precursor maintained stable and the pyrolysis had not occurred yet. The reason of weight loss might be the evaporation of water (m/z: 18).

Stage 2: Pyrolysis of the polymer (250~800 °C, weight loss of 44.7%). Weight decreased dramatically in this temperature range, mainly due to the pyrolysis of the polymer and the formation of volatile small molecules, such as CH₄ (m/z: 16), CHₓ (x=2 or 3, m/z=14 or 15) and SiO (m/z=44).

According to the MS curve, this stage could be subdivided into three phases:

1) 250~450 °C, weight loss of 33.0%. Massive breakage of Si-CH₃ bonds produced substantial active methyl radicals, which then formed methane (CH₄, m/z=16) and Si-CH₂ by the reactions as follows.

\[ \text{Si–CH}_3 \rightarrow \text{Si} + \text{CH}_3 \]
\[ \text{CH}_3 + \text{Si–CH}_3 \rightarrow \text{Si–CH}_2 + \text{CH}_4 \]
Moreover, the rupture of C_{ipso}-Si bonds produced a small amount of volatile ferrocene (Fc, m/z=184~186) and SiO (m/z=44).

(2) 450~600°C, weight loss of 29.7%. The release of ferrocene was complete in this temperature range. The weight loss could be attributed to the formation of some small molecules by the breakage of remain Si-CH\textsubscript{3}.

(3) 600~800°C, weight loss of 2.0%. The major reason of the weight loss was the release of H\textsubscript{2} (m/z=2) from the reaction of methyl radicals.

Stage 3: Completion of pyrolysis (800~1000°C, weight loss of 3.3%). Pyrolysis of the polymer completed mostly, reaching stable inorganic state. Weight loss was mainly due to the reaction between free carbon and remain oxygen to generate CO(m/z=28).

The crystallization process of the preceramic sample as the temperature increased was also monitored. The preceramic polymer was put on a metal specimen mount, which was then heated at a speed of 10 °C/min under vacuum in the sample chamber of XRD spectrometer. The XRD patterns of products pyrolyzed at various temperatures are shown in Fig. 4. The peaks at 2\theta = 39.6°, 46.1°, 67.3°, and 81.1° in all of the spectra could be attributed to diffraction of the metal specimen mount. As can be seen in Fig. 4, there was no diffraction peaks detected at 400 °C, denoting that the product was amorphous at this temperature. However, peaks at the diffraction angle of 26°, 44.7°, 65.1° and 82.4° appeared, which became stronger and sharper gradually as the sintering temperature ascended from 500°C to 1000°C. Specifically, the peaks at 2\theta = 44.7° (1 1 0), 65.1° (2 0 0) and 82.4° (2 1 1) were attributed to \alpha-Fe (JCPDS PDF 06-0696)[27], while the peak at 2\theta=26° was assigned to graphite.

XPS spectra of Fe/Si/C ceramic powder sintered at 900 °C under an atmosphere of N\textsubscript{2} is displayed in Fig. 5. Four characteristic peaks could be seen clearly in the spectra, corresponding to Si\textsubscript{2p}, C\textsubscript{1s}, O\textsubscript{1s} and Fe\textsubscript{2p}, with atom content of 6.96%, 78.67%, 13.5%
and 0.86%, respectively. According to the XPS data (ESI, Table S1), it could be inferred that the ceramic powder contained Fe in the form of Fe(III) and elemental iron. Additionally, the fitting curve of carbon indicated that carbon existed in diverse forms but mainly as free carbon in the ceramics, while silicon was in the form of SiO₂ and amorphous SiCₓOᵧ. The existence of O in the ceramics may be produced by the introduction of few oxygen and moisture absorbed by the precursor polymer to the pyrolytic process.

3.3. The influence of pyrolytic atmosphere

XRD patterns of ceramic products sintered at 900°C under atmospheres of N₂, air and NH₃ can be seen from Fig. 6. The main components in ceramic product sintered at 900 °C under air were γ-Fe₂O₃ and carbon. On account of the oxygen in air, Fe in the ceramic thereby appeared as γ-Fe₂O₃. Whereas for the ceramic products sintered under NH₃, only diffraction peaks of α-Fe existed, which was probably due to the deoxidation of iron from its oxidation states to its elemental state. In other words, the oxidation of iron was prevented by NH₃. Compared with the ceramics sintered under N₂, there was no carbon appeared in the product under NH₃. The free carbon produced with the increment of heating temperature was probably consumed by the reaction with active NH₃.

XPS spectrum of Fe/Si/C ceramics sintered at 900 °C under air is shown in Fig. 7 (a). Four characteristic peaks attributed to Si 2p, C 1s, O 1s and Fe 2p indicated that the atom contents were 6.96%, 78.67%, 13.5% and 0.86%, respectively. The bond energies for Fe 2p from the spectra fitting were obtained as 713.7 eV (Fe 2p₃/₂) and 726.5 eV (Fe 2p₃/₂), which were much higher than their counterparts in γ-Fe₂O₃. Possibly, the magnetism of the ceramic product detrimental to XPS analysis was to blame for such deviation. As can be seen in Fig. 7 (b), for the ceramic product sintered under NH₃ at
900°C, the five peaks related to Si 2p, C 1s, N 1s, O 1s and Fe 2p implied that the atom contents of each element were 15.7%, 46.7%, 3.9%, 32.0% and 1.6%, respectively. Surprisingly, the ceramics sintered under NH₃ contained such a large amount of O from the analysis of XPS, which was not observed in XRD pattern. It is well known that the precise amount of elemental content can hardly be measured by the normal analysis of XPS. Therefore, in order to further determine the composition of ceramic products quantificationally sintered under different atmospheres, chemical elemental analysis was used and the results are shown in Table 1. There were not obvious differences in the content of Si of the ceramics obtained under different atmospheres, however, air consumed much more C than NH₃ resulting in ceramics of only 0.4 wt% carbon, which agreed well with the XRD analysis. The proportion of Fe was the least in the ceramics sintered under N₂. There was O of 38.7 wt% in the ceramics sintered in air, which was 21.2 wt% under NH₃. The appearance of O in the ceramics may be produced by the introduction of few oxygen and moisture absorbed by the precursor polymer to the pyrolytic process. However, the O must exist in amorphous state as there was no obvious diffraction peak of any oxides in the XRD pattern of the ceramics. The existence of N in the ceramics obtained under NH₃ confirmed the reaction of the atmosphere during the pyrolytic process of the preceramic polymer.

Magnetic properties of products sintered under various atmospheres were investigated, hence the plots of magnetization versus applied magnetic field can be seen in Fig. 8, and the magnetic properties of ceramics are shown in Table 2. The results proved that all of the three ceramic products were ferromagnetic, with low magnetic remanence (Mr) and coercivity (Hc). The ceramic product sintered under NH₃ revealed the largest saturation magnetization of 65.6 emu/g particularly, which was probably due
to the huge saturation magnetization of $\alpha$-Fe (Ms=218 emu/g) and the large content of iron in this product sintered under NH$_3$.

3.4. The influence of heating rate

As illustrated by the aforementioned result, NH$_3$ atmosphere had tremendous influence on the composition and structure of Fe/Si/C ceramics, and played a significant role in improving the magnetic properties of the corresponding ceramics. Accordingly, efforts were devoted to explore the composition, structure and property of ceramics obtained under the same atmosphere of NH$_3$ but at different heating rates. Two polymer precursor samples were put into a quartz tube furnace, which were heated to 900 °C and kept at this temperature for 2 h. The heating rate was the same as 3 °C/min for the two samples except for the temperature range of 400~600 °C, which was 2/3 °C/min and 3 °C/min, respectively.

Fig. 9 shows the XRD spectra of products sintered with heating rates of 2/3 and 3 °C/min. The diffraction peaks at 41.1° (1 1 1), 47.9° (2 0 0) and 84.7° (3 1 1) attributed to $\gamma'$-Fe$_3$N[28] could be observed clearly in the pattern of ceramics obtained with the heating rate of 2/3 °C/min. Furthermore, the intensity ratio of diffraction peaks I(2 0 0)/I(1 1 1) was 0.89, exceeding that of the standard card (0.554), which indicated a crystalline growth along (2 0 0). Although reported in the literatures[29,30], Fe$_3$O$_4$ could be reduced to Fe$_3$N under a mixed atmosphere of NH$_3$ and H$_2$, in this experiment there appeared diffraction peaks of Fe$_3$O$_4$ under the atmosphere of NH$_3$. Whereas for the ceramic products sintered under NH$_3$ at a rate of 3 °C/min, only diffraction peaks of $\alpha$-Fe existed.

As seen from the Fe 2p photoelectron spectra (Fig. 10) of ceramics sintered with different heating rates, a significant increment of $\alpha$-Fe was witnessed in ceramics sintered with the slower heating rate. Presumably, the slower heating rate may cause
more sufficient pyrolytic reaction, leading to iron existing in the ceramics mainly as its elemental state. Still, irons of high oxidation states existed in the ceramics, possibly because of the rapid oxidization by the oxygen and moisture absorbed on the surface of the precursor during the ceramization.

The plots of magnetization versus applied magnetic field, as shown in Fig. 11, suggested that the Ms, Mr, and Hc of ceramics sintered under NH$_3$ at 900 °C with a heating rate of 2/3°C/min was 80.5 emu/g, 3.7 emu/g, and 0.13 kOe, respectively. Obviously, the saturation magnetization ascended (22.7%), which was mainly due to the different existence forms of iron.

4. Conclusion

The preparation of polymer-derived Fe/Si/C ceramics was achieved by the synthesis and pyrolysis of the preceramic hyperbranched polyferrocenylsilane. The pyrolytic temperature was essential to the ceramization of the precursor and the formation of the Fe/Si/C ceramics. The polymer maintained stable and pyrolysis had not occurred below 250 °C. However, the volatiles such as H$_2$, CH$_4$, SiO and ferrocene were released among 250~800 °C with a weight loss of ~60% due to the pyrolysis and rearrangement of the polymer skeleton and Si-CH$_3$ bonds. Pyrolysis of the polymer completed among 800~1000 °C, reaching almost stable inorganic state. However, the crystallization of the pyrolytic product started at 500 °C. The atmosphere and heating rate also played important roles in the composition and magnetic properties of the corresponding Fe/Si/C ceramics. Fe existed as $\alpha$-Fe in ceramics sintered at 900 °C under N$_2$ and NH$_3$ atmospheres. However, the main components in ceramic product sintered under air were $\gamma$-Fe$_2$O$_3$ and carbon. Although all of the three ceramic products were ferromagnetic with low remanent magnetization and coercivity, However, the results showed that NH$_3$ atmosphere played a significant role in improving the magnetic properties of the
corresponding ceramics. The ceramic product sintered under NH₃ revealed the largest saturation magnetization of 65.6 emu/g in particular. Obviously, the saturation magnetization further ascended (22.7%), when the magnetic Fe/Si/C ceramics was obtained under NH₃ with a slower heating rate, in which Fe existed as α-Fe, Fe₃O₄ and γ′-Fe₃N.

Acknowledgments

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References


Figure Captions

Scheme 1 Synthetic route of hyperbranched precursor

Fig.1. ¹H-NMR(a, in CDCl₃) and FT-IR(b) spectra of the polymer precursor

Fig. 2. GPC pattern (a) and TG curve (b) of precursor

Fig. 3. TG-MS spectra of hyperbranched polyferrocenylsilane

Fig. 4. XRD patterns of products pyrolyzed at various temperatures

Fig. 5. XPS spectra of ceramic powder sintered at 900 °C in N₂

Fig. 6. XRD patterns of products sintered under various atmospheres

Fig. 7. XPS spectra of ceramic powder sintered at 900°C under air (a) and NH₃ (b).

Fig. 8. Magnetization plots of ceramic products sintered under different atmospheres

Fig. 9. XRD patterns of ceramic products sintered with different heating rates

Fig. 10. Fe 2p photoelectron spectra of ceramics sintered with various heating rates

Fig. 11. Magnetization plots of ceramic products sintered with different heating rates

Tables
Table 1  Chemical composition of ceramic sintered under different atmospheres

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Table 2  Magnetic properties of ceramics sintered under different atmospheres

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<th>Mr (emu/g)</th>
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