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Article

Crystallization Behavior and Controlling Mechanism of Iron-Containing Si–C–N Ceramics

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The crystallization behavior and controlling mechanism of the Si–Fe–C–N system based on polymer-derived SiCN ceramic filled with iron metal powder has been studied. The composite preparation conditions allow the formation of a random distribution of metallic particles in the polymer matrix volume for the Si–C–N system. Pyrolysis of the composite material at 1100 °C indicates the presence of one crystalline phase Fe_3Si. While the sample pyrolyzed at 1200 °C reveals the formation of both Fe_3Si and Fe_5Si_3 phases, a crystallization of β–SiC is additionally observed by increasing the temperature up to 1300 °C. The propensity for the formation of SiC is due to the presence of Fe_5Si_3, where a solid–liquid–solid (SLS) growth mechanism was suggested to occur. X-ray diffraction (XRD), scanning electron microscopy (SEM), differential thermal analysis (DTA), and thermal gravimetric analysis with mass spectroscopic detection (TGA-MS) were employed to investigate the crystallization behavior of the Si–Fe–C–N system.

I. Introduction

Polymer-derived ceramics (PDCs) have gained a remarkable interest in the last two decades as precursors for ceramic materials possessing improved and novel properties compared to conventional ceramics.[1,2] PDCs based on the ternary Si–C–N-system have been reported to exhibit extraordinary high temperature properties. They are basically X-ray amorphous and do not crystallize up to 1400–1500 °C.[3,4] They withstand oxidation up to 1600 °C and do not show any significant mechanical creep at this temperature level.[5] Chemical modifications of the polymeric precursors with transition metal (e.g., Co, Fe) are of interest for many fields of engineering because of their interesting electrical, magnetic, and catalytic properties. Such composite material Si–C–Fe–N cannot be prepared by the traditional method of high temperature and high pressure sintering. As an alternative, a powder processing route with an organometallic precursor to prepare metal-containing SiCN can be envisaged as it offers several advantages including initiation of solid state reactions at lower temperature and improved control over composition, microstructure, and final form of the expected material. The achievement of metallic properties in such composites depends on many factors, and it is just the possibility of controlling the crystallization behavior, physical, and electrical characteristics which determines the variety of ranges of their application. Most work on polymer-derived ceramics has focused on the design, synthesis, and pyrolysis of precursors, for example, polysilazanes, polycarbosilanes, polysiloxanes, polysilylcarbodiimides, under inert atmosphere to produce amorphous SiCN and SiOC-containing ceramic rather than phase evolution and microstructure of metal-containing ceramic network.[6–11]

Saha et al.[12] reported for instance the synthesis of iron modified Si–C–N ceramics by incorporating Fe_3O_4 into the liquid polysilazane and subsequent pyrolysis up to 1100 °C in a nitrogen atmosphere. The evolution of CH_4 and H_2, in the 600–900 °C range reduces the ferritic iron oxide into α-iron creating a high-temperature magnetic material for applications in harsh environments. Others[13] indicated that the pyrolysis of a cross-linked polysilazane filled with $FeCl_2$ at

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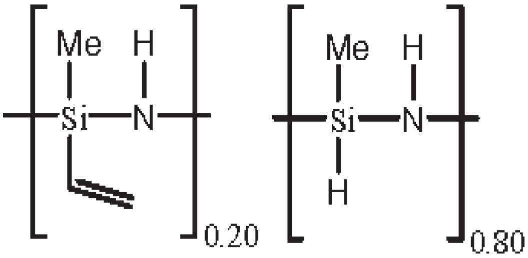

Figure 1. Molecular structure of the polysilazane20 (Ceraset) polymer provided by the KiON company.

1700 °C in N_2 atmosphere leads to the growth of silicon carbide nanorods, being generated because of a solid−liquid−solid (SLS) mechanism resulting from the reaction of the amorphous SiCN phase with Fe to form a liquid Si−Fe−C alloy. More recently, we reported the pyrolytic conversion of a polysilazane blended with iron or iron carbonyl in argon atmosphere to obtain a magnetic Si−Fe−C−N ceramic.[14] This earlier communication was mainly focused on the magnetic property and phase evolution of iron and cobalt-containing SiCN at 1100 °C. However, this current investigation provides a basis for certain conclusions on the effect of heat treatment on the mechanism and crystallization behavior of an iron-filled cross-linked polysilazane up to 1300 °C. Until now, no study has been made as regards the influence of the iron addition on the composition of the amorphous SiCN inorganic product. For these reasons, the phase evolution of a liquid Ceraset/Fe mixture was studied from room temperature (RT) to 1450 °C using differential thermal analysis (DTA) and thermo-gravimetric with mass spectrometry techniques (TGA-MS) to analyze the gases produced as well as the crystallization behavior of the composite.

II. Experimental Procedure

For the preparation of the iron-containing polymer-derived SiCN ceramic, a commercially available polysilazane20, Ceraset from Kion Inc., U.S.A. and elemental iron powder from Alfa Aesar Co. were used. The molecular structure of the polysilazane20 is shown in Figure 1. It is a liquid sensitive to moisture and oxygen and has to be manipulated under protective atmosphere. The polysilazane was cross-linked at 280 °C for 5 h in a vertical tube furnace (Fa. GERO, Germany), milled using a planet ball mill (30 min at 180 rpm), sieved through a 100 μm, and mixed with 10 vol % Fe powder. The iron powder has a purity $\geq$99.9% and a particle size of 10 μm. The polymer-to-ceramic transformation of both pure Ceraset and iron-containing Ceraset were followed by means of simultaneous TG/DTA coupled with mass spectroscopic detection using Netzsch STA 449C *Jupiter* instrument, Germany. The measurements were done under flowing argon (25 mL/min), with a heating rate of 5 °C/min from ambient temperature up to 1450 °C.

Si−Fe−C−N bulk samples were prepared by warm pressing the cross-linked Ceraset/iron mixture at 200 °C for 60 min (P/O Weber warm press, pellets of 12 mm diameter) followed by pyrolysis at 1100, 1200, and 1300 °C in argon atmosphere for 5 h. X-ray diffraction (XRD) data for the samples were collected with a STOE STADI-P powder diffractometer, using monochromatic Mo $K_{\alpha 1}$ radiation. The overall microstructure characterization was performed using high-resolution scanning electron microscopy (HRSEM) coupled with EDX (Philips XL 30 FEG with EDAX CDU LEAP detector).

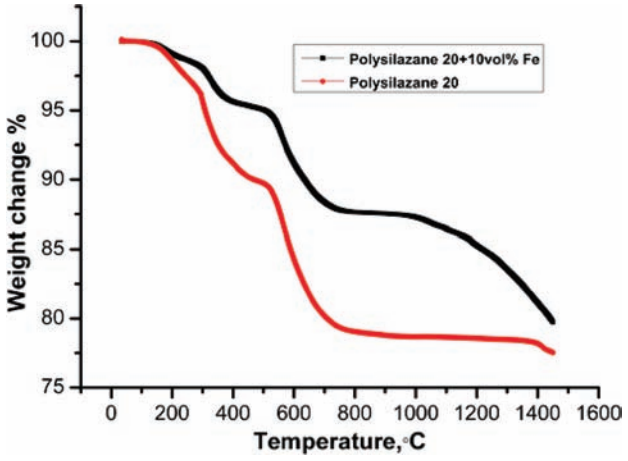

Figure 2. TG profiles of the pure polysilazane and polysilazane + 10 vol %Fe pyrolyzed under Ar.

III. Results and Discussion

TGA study, at 5 °C min^{-1} under Ar flow, of the iron filled polysilazane reveals a ceramic yield of ~87% at 1100 °C, compared to only ~77% for pure Ceraset, Figure 2. TGA of pure Ceraset shows that the majority of weight loss happens between 200 and 750 °C.

Mass spectrometry (MS), Figure 3, indicates that the gaseous phases generated correspond to evaporating monomer or oligomer fragments with m/e = 41−44, and to CH_4, **NH_3**, H_2O with m/e = 16−18 and finally to H_2 with m/e = 2 as well as to other organic components.

Four main regions are present in the TGA curve of iron-filled polysilazane: (1) from 128 to 300 °C, an initial 1.32% mass loss is observed; (2) from 300 to 530 °C, an additional 3.26% mass loss occurs; (3) from 530 to 840 °C, the mass loss is increased to 7.69% followed by a small plateau; (4) above 986 °C a decreasing slope of the curve with a mass loss of ~8% is observed. The mass loss in the first 2 regions is assigned mainly to the evolution of organic components and cross-linking processes[15] accompanied by the release of ammonia as observed by the in situ mass spectrometry Figure 4. The third mass loss value (7.69%) is mainly due to the evolution of methane, ammonia, carbon dioxide, and water. The detection of CO_2 and **H_2O** by MS might be due to the oxidation of methane.

As apparent from the TGA-MS in Figures 2−4, the iron filled polysilazane reveals a weight loss of ~13% up to 840 °C. It also exhibits a noticeable weight loss of ~8% upon heating up to 1450 °C which most likely originated from SiO. However, an ionized group with mass of 12, 28, and 44 is observed which could be resulting from the evolution of carbon monoxide and carbon dioxide. Oxygen, which allows CO, H_2O, and CO_2 to be produced, originates either from the material itself (oxygen contained in the polysilazane precursor) or from an external source such as the flowing argon gas. As a consequence, the presence of oxygen in the system

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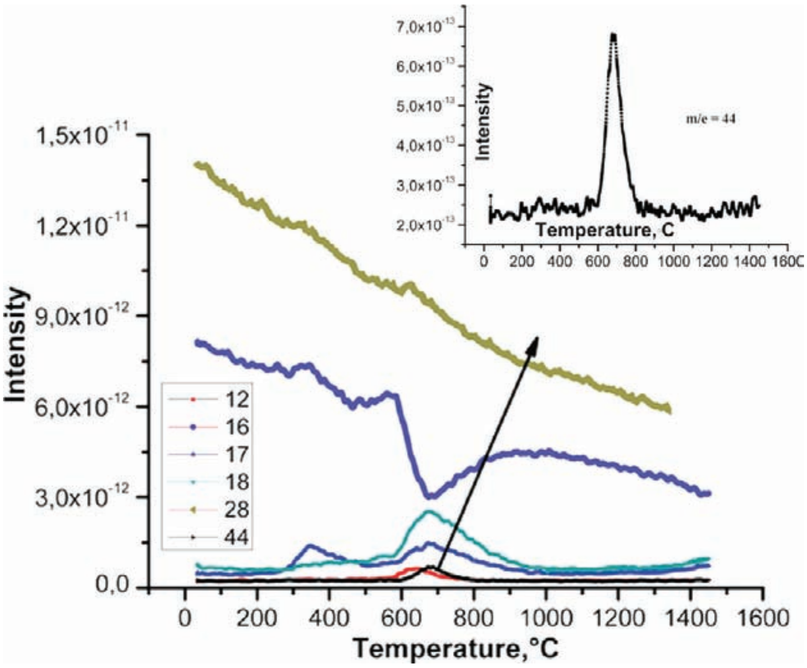

Figure 3. MS analysis of the pure polysilazane heat-treated under Ar up to 1450 °C. An enlargement view of the MS of $m/e = 44$ is shown (black 44, orange 12, blue 17, olive green 28, dark blue 16, gray 18).

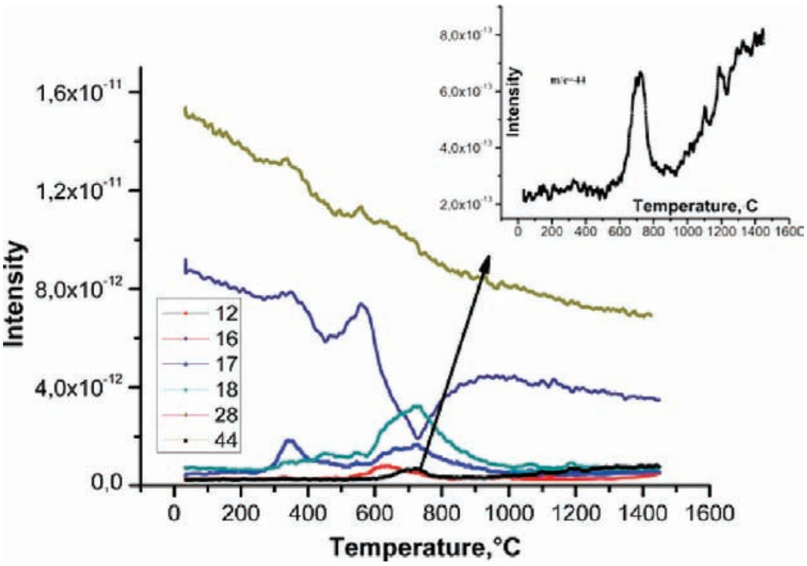

Figure 4. MS analysis of the iron-containing polysilazane up to 1450 °C under Ar. An enlargement view of the MS of $m/e = 44$ is shown (black 44, orange 12, blue 17, olive green 28, dark blue 16, gray 18).

results in a partial oxidation of silicon and finally at temperature above 1150 °C, and because of the molten state of iron silicides, a reduction might occur with the evolution of SiO and CO. It is clear from the inset in Figure 4 that the evolution of SiO ($m/e = 44$) does happen during the melting process of silicides.

The DTA study of the two precursors is presented in Figure 5. As expected, the pure polysilazane does not show any crystallization behavior, while the iron-filled polysilazane displays first an endothermic peak at 720 °C, corresponding mainly to the departure of methane, water vapor, and carbon dioxide from the material, accompanied with shrinkage and embedding of iron within the SiCN matrix. An exothermic peak centered at 1058 °C is assigned to the crystallization of Fe_3Si, as revealed by XRD after pyrolysis at 1100 °C, Figure 6, followed immediately by two successive endothermic peaks at 1166 and 1200 °C. These two peaks belong to the melting points of Fe_3Si and Fe_5Si_3. An enlarged DTA chart of the iron-filled polysilazane is also given in Figure 5.

It has been reported by Pan et al.[16] that the melting point of iron silicides, for example, Fe_3Si and Fe_5Si_3, obtained from the Fe−Si phase diagram, are within the range 1210−1300 °C and they exhibit good wettabilities to SiC at temperatures above their melting points. The XRD of the sample pyrolyzed at 1200 °C showed the presence of both Fe_3Si and

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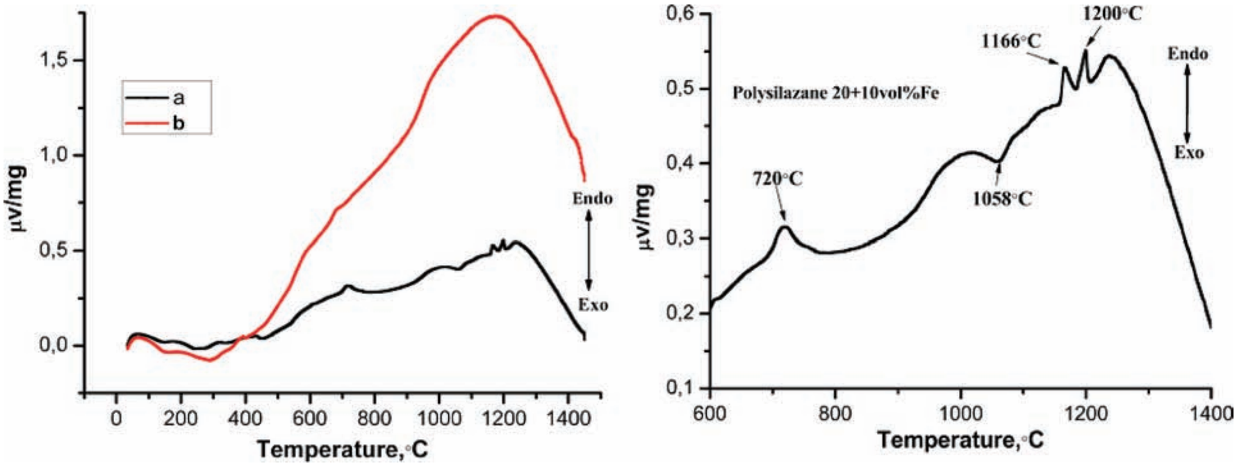

Figure 5. DTA study of (a) pure polysilazane and (b) polysilazane + 10 vol % Fe pyrolyzed up to 1450 °C under Ar.

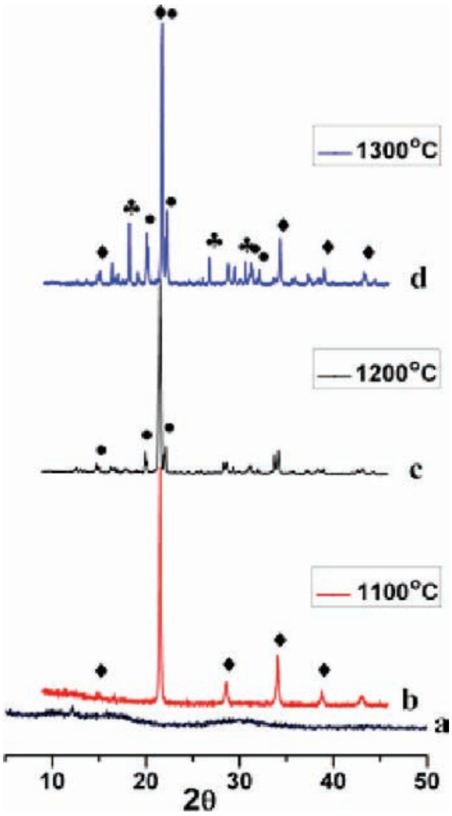

Figure 6. XRD patterns of (a) cross-linked polysilazane at 1300 °C, (b) cross-linked polysilazane + 10 vol % Fe at 1100 °C, (c) cross-linked Ceraset + 10 vol % Fe pyrolyzed at 1200 °C, (d) cross-linked Ceraset + 10 vol % Fe pyrolyzed at 1300 °C under Ar atmosphere [clover leaf = ***β*-SiC**, diamond = Fe_3Si, and circle = Fe_5Si_3].

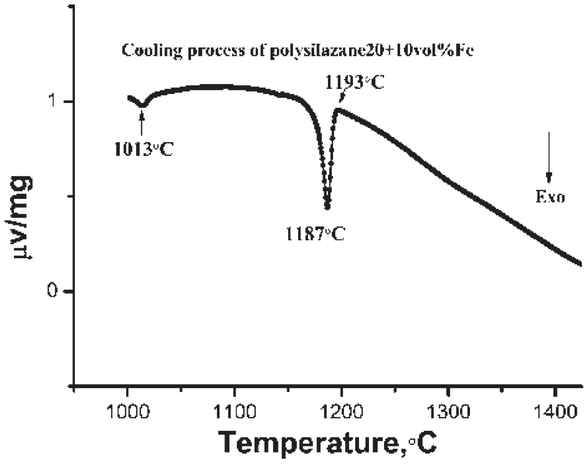

Figure 7. DTA cooling profile of iron-filled polysilazane.

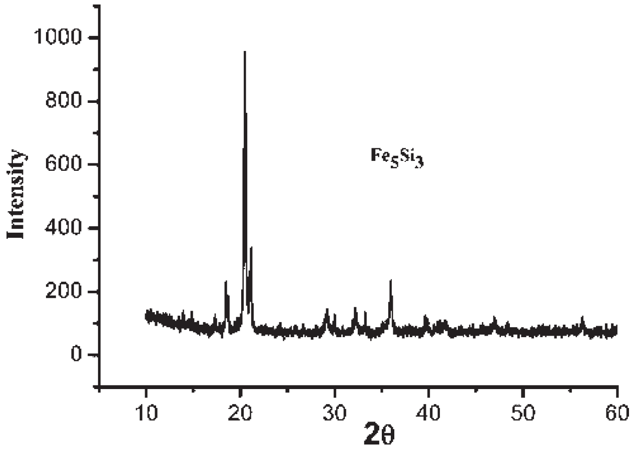

Figure 8. XRD of the shiny sphere of Fe_5Si_3 separated after pyrolysis at 1300 °C.

Fe_5Si_3 crystalline phases. Further heating up to 1300 °C highlighted the formation of another major peak assigned for ***β*-SiC**, Figure 6.

The formation of silicon carbide out of a SiCN matrix at this temperature is quite unusual, as the crystallization of SiC from polymer-derived SiCN materials was reported to occur at temperatures above 1500−1600 °C.[17,18] The crystallization of SiC starts at 1193 °C during the cooling process of the iron-filled polysilazane Figure 7, while the exothermic peak at 1013 °C referred mainly to the separation and solidification of the liquid phase Fe_5Si_3 as a small shiny sphere. This was supported by XRD in Figure 8

Iron and silicon in their solid-solution series produce a rich variety of binary compounds with a wide range of magnetic,

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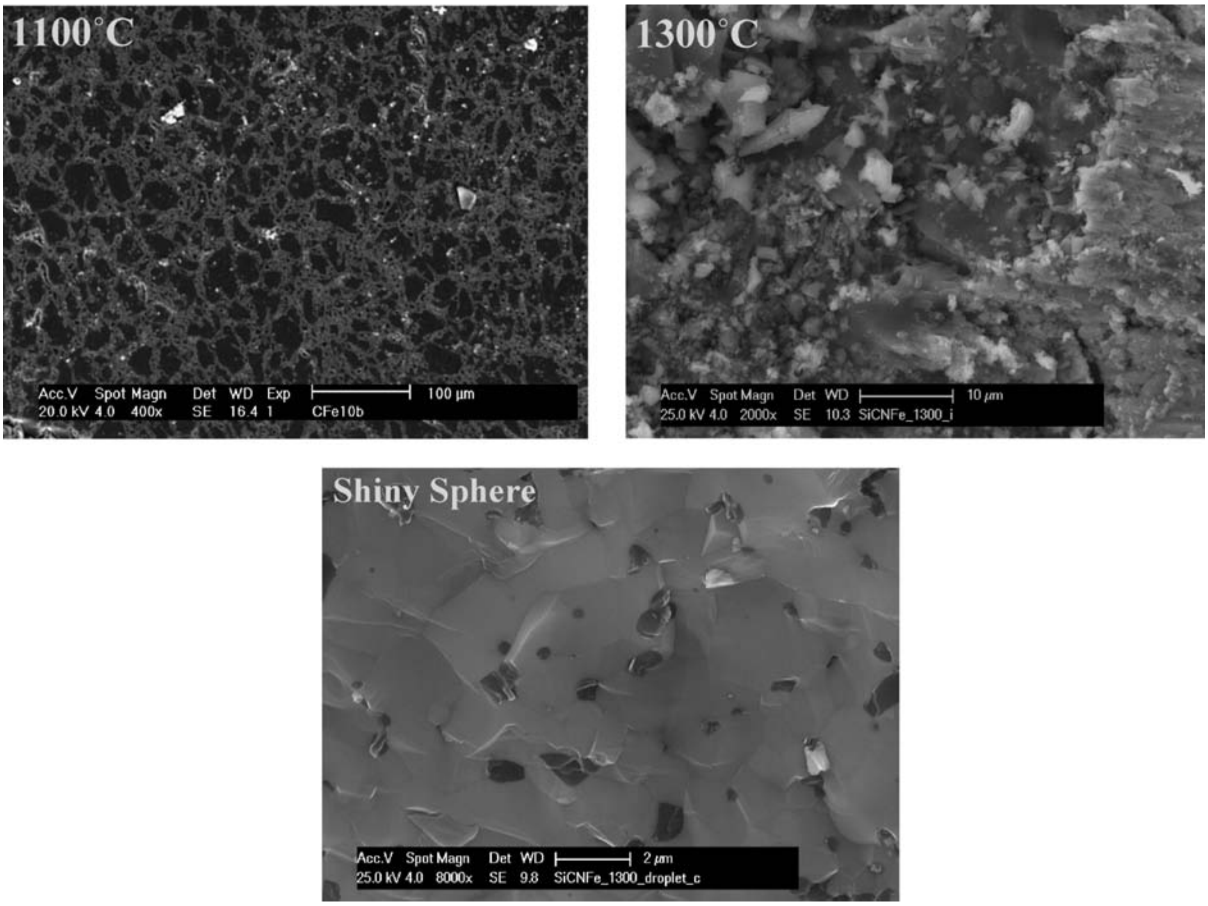

Figure 9. SEM micrographs of Si−Fe−C−N samples pyrolyzed at 1100 and 1300 °C as well as of the solidified shiny sphere.

electrical, and optical properties.[19] Recently, it was found that Fe_3Si was the main ferromagnetic phase obtained during the pyrolysis of iron containing SiCN at 1100 °C.[14] Of these and from the standpoint of developing a random access memory (RAM) material and for application in terms of electromagnetic (EM) absorption, the Fe_3Si is the most desirable.

We can conclude that, at the beginning of the process, the amorphous SiCN phase reacted with Fe to crystallize Fe_3Si at 1100 °C, and then by increasing the temperature up to 1300 °C, a liquid phase of Fe−Si−C alloy is then probably formed. Once the liquid phase became saturated in Si and C atoms, precipitation occurred, giving rise to SiC nuclei and solidification of Fe_5Si_3. On the basis of these circumstances, we suggest a SLS growth mechanism for the crystallization of SiC. The work of Jha et al.[20] pointed out that the addition of either silicon (Si) in an Fe−C melt or carbon (C) in an Fe−Si melt results in a substantial decrease in the surface tension of the liquid−SiC interface, which provides a lower energy barrier for nucleation of SiC. This is not surprising as there has been evidence reported by some authors[21−23] that a carbon saturated Fe−Si liquid alloy can exist below 1250 °C. Moreover, Bootsma et al.[24] have mentioned that the alloy composition Fe−Si−C could be an eutectic liquid having an invariant temperature at around 1200 °C. Furthermore, Chrysanthou and his co-authors[25] have calculated the liquidus curve in a FeSi−SiC pseudo binary system and determined the eutectic temperature at 1165 °C, indicating a low temperature Fe−Si−C liquid. The study on the growth of SiC from iron silicide fluxes showed that Fe_5Si_3 favors the precipitation of silicon carbide, while Fe_3Si rather lead to carbon precipitation instead of SiC formation[26].

To further support the SLS mechanism for the formation of silicon carbide; scanning electron microscopy (SEM) investigations were performed on Si−Fe−C−N samples pyrolyzed at 1100 and 1300 °C, Figure 9. They showed a microstructure consisting of iron-rich (bright) and iron-poor (dark) regions as analyzed by EDX. The homogeneity of iron particle distribution within the whole matrix leads to the conclusion that the observed microstructure is a result of chemical reactions and transport processes during the polymer to ceramic transformation.[14] On the contrary, distributing the same volume of metal particles in a matrix pyrolyzed at 1300 °C rather promote the formation of another silicide phase Fe_5Si_3. This is a weak zone that usually constitutes fracture initiation sites because of the molten state of the silicides that results in the separation of shiny sphere Fe_5Si_3

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and crystallization of silicon carbide. XRD analysis of the small shiny sphere shows mainly the presence of Fe_5Si_3 as illustrated in Figure 8. SEM of the shiny sphere reveals the absence of porosity in accordance with the suggestion of a SLS growth mechanism.

Conclusion

The pyrolysis of organometallic polymers containing a transition metal group (M) is an efficient route for preparing Si-M−C−N ceramic. The introduction of iron in the chain of the cross-linked polysilazane allowed the formation of the Fe_3Si phase with good yields by pyrolysis at 1100 °C in argon stream. Crystallinity increased when the heat treatment was done at 1300 °C, and the crystalline phases are Fe_3Si, Fe_5Si_3, and SiC. The crystallization of SiC was assumed to occur from the liquid Fe−Si−C alloy being formed during the molten state of silicides at 1300 °C. At a temperature of 1100 °C, a solid state reaction was found to occur promoting the formation of Fe_3Si, while the unexpected crystallization of SiC at 1300 °C is attributed to a SLS mechanism because of the formation of the liquid alloy.

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