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Low temperature in situ formation of cobalt in silicon nitride toward functional nitride nanocomposites†

Shotaro Tada, a Maira Debarba Mallmann, bc Haruna Takagi, a Junya Iihama, a Norifumi Asakuma, a Toru Asaka, a Yusuke Daiko, a Sawao Honda, a Rafael Kenji Nishihora, bc Ricardo Antonio Francisco Machado, c Samuel Bernard b and Yuji Iwamoto *a

This work highlights the first demonstration of a low-temperature in situ formation of Co nanocrystallites embedded within an amorphous silicon nitride matrix through careful control of the chemistry behind material design using perhydropolysilazane (PHPS) as a Si3N4 precursor further coordinated with CoCl2 and ammonia as a pyrolysis atmosphere. The Co nucleation was allowed to proceed at temperatures as low as 400 °C via thermal decomposition of Co3N pre-formed in situ by the reaction of CoCl2 with the Si centers of PHPS at the early stage of pyrolysis (220–350 °C).

Material discovery is a key element in the innovation cycle of energy conversion, transmission and storage technologies. In this category of energy-focused materials, advanced ceramics appear to be high value-added products with performances that are tailored via their rational and elaborate designs. Ceramic processing methods based on molecular engineering and precursor chemistry are well appropriate approaches to design such materials that can reach performances far beyond those developed by more conventional synthesis routes. A very convenient precursor route is the polymer derived ceramics (PDCs) route which allows fine control over the chemical composition of the final ceramic materials as well as their phase distribution and nanostructure. This offers enhanced or novel functional properties which have been recently highlighted in metal/Si-based (oxy-)carbide and carbonitride matrix composites such as Ni/SiC, Ni/SiOC, Ni/SiCN(O) and M/SiCN (M = Pd, Ru, PdRu, Cu, Ir, Ni, Pt, Co, Fe) derived from metal-modified polycarbosilanes, polysiloxanes and polysilazanes, respectively. In particular, as reported by Kempe et al., the polymer-derived M/SiC nanocomposites are attractive as robust and reusable catalysts which can be applied to various catalytic reactions by changing the metal nanoparticle component: dehydrogenation by Pd, hydrogenation and dehydrogenation of N-heterocycles by PdRu; selective hydrocarbon oxidation by Cu; dehydrogenative condensation of secondary alcohols and 1,2-amino alcohols by Ir; chemoselective hydrogenation of ni troarenes by Ni, Co and Fe, and hydrolysis of sodium borohydride by Pt.

In contrast, the design of metal/Si-based composites in nitride matrix systems (i.e., M/Si3N4) has never been demonstrated and it remains highly challenging while nitrides can be particularly interesting for catalysis as a support and/or as a catalyst itself. This is mainly caused by the reactivity of the central metal cations distributed in the polysilazane network with ammonia (used as atmosphere to form Si3N4 from polysilazanes) forming a metal nitride nanophas e distributed in the Si3N4 matrix. This observation is well illustrated in the recent reports on Si3N4-based nanocomposites including TiN/Si3N4 and VN/Si3N4 compounds. Among them, the TiN/Si3N4 nanocomposites exhibited strong synergy with Pt nanoparticles, which were homogeneously deposited in a secondary synthesis step onto the nanocomposite support. This resulted in excellent catalytic performance for dehydrogenation of sodium borohydride in water. Thus, this report confirmed the attractiveness of nitrides for catalysis. To simplify this two-step process, and avoid the use of precious metals such as Pt while forming Si3N4 supporting the catalytically active phase (i.e., M/Si3N4) in a one-step process, we describe the coordination of a polysilazane (PHPS) with cobalt chloride (CoCl2) allowing the in situ formation of Co during the further thermo-chemical conversion of the PHPS into Si3N4 in flowing ammonia. The unique low-temperature in situ formation of Co within the Si3N4 matrix is discussed based on a complete set of characterization techniques including elemental analyses, X-ray diffraction (XRD), thermogravimetric – mass spectrometric (TG–MS) analyses, infrared spectroscopy, ultraviolet-visible (UV-Vis) spectroscopy and transmission electron microscopy.

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(TEM) observations. The basis of our approach comes first from the design of a suitable highly pure synthetic precursor in which uniform chemical composition is established at a molecular scale. Thus, we mixed CoCl₂ with PHPS which only contains Si, N and H elements in a controlled Co/Si molar ratio of 0.2 to form a compound labeled Co-PHPS. The synthesis is performed in toluene and directed to keep a homogeneous distribution of CoCl₂ throughout the PHPS network (without direct reaction). Then, the precursor is heat-treated under ammonia to form an unstable (thermally) metal nitride phase at low temperatures, while avoiding the formation of free Si at higher temperatures as known using PHPS,₃₅,₃₆ thus leading to Co/SiNₓ compounds at low and intermediate temperatures as discussed below.

Pyrolysis leads to samples labeled as Co/SiNX (X being the temperature at which the material has been heat-treated) with tuned phase composition and nano-/microstructure organization according to the pyrolysis temperature. The chemical compositions of the Co/SiNX samples are listed in Table 1. All the procedures for Co-PHPS synthesis, subsequent heat treatment and characterization of Co/SiNX are reported in the ESI.†

Chemical compositions of the Co/SiNX samples are discussed in relation to their XRD patterns (Fig. 1), TG–MS experiments (Fig. 2) and FTIR spectroscopy (Fig. 3). The Co/SiN400 sample exhibits three characteristic diffraction peaks assigned to a-Co (JCPDS No. 00-015-0806 at 2θ = 48.6, 52.0, and 55.61) along with a residual component of CoCl₂ (JCPDS No. 01-085-0446) and NH₄Cl (JCPDS No. 01-073-0365). Additionally, two small diffraction peaks appear at 2θ angles of 46.5 and 50.41, indicating the formation of cobalt nitride (Co,N. JCPDS No. 04-004-4638). Then, at 500 1C (Co/SiN500 sample), the Co₂N disappears while the metallic a-Co forms. At 800 1C (Co/SiN800 sample), two distinct diffraction peaks appear at 51.8 and 60.71, which are assigned to b-Co (JCPDS No. 01-089-4308) along with a-Co, and several minor peaks related to both a- and b-Si₃N₄ were also identified. The NH₄Cl XRD peaks disappeared because of its vaporization when heated above 500 1C; this was confirmed by its condensation in the cool parts (extremities) of the furnace tube. Finally, the Co/SiN1000 sample exhibits the formation of thermodynamically favorable cobalt silicide (Co₂Si, JCPDS No. 01-089-4181) in addition to the a- and b-Si₃N₄ phases. Thus, Co/SiN₄ (amorphous and crystalline) composites are generated at temperatures below 800 1C. In order to investigate this low-temperature in situ formation of a/b-Co, TG–MS analyses have been performed. The TG-curve (Fig. 2a) exhibits two main weight loss regions at 50–220 1C and 220–350 1C. The coupled MS analysis reveals that the main evolved component at 50–220 1C is toluene (C₆H₅CH₃. m/z = 91, Fig. 2b) as the reaction solvent medium, while at 220–350 1C, the dominant gaseous species are chloride fragments, such as hydrochloric acid (HCl, m/z = 36 and 38, Fig. 2c), monochlorosilane (m/z = 64 and 66, Fig. 2d) and dichlorosilane (m/z = 99 and 101, Fig. 2e) species.

Table 1 Chemical composition of the Co/SiNX samples

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition/wt%</th>
<th>Composition/at%</th>
<th>Atomic ratio to Si</th>
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<tr>
<td></td>
<td>EDS (Co/Si ratio)</td>
<td>Elemental analysis</td>
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<tr>
<td>Co/SiN400</td>
<td>44.83 35.23 0.80 16.84</td>
<td>2.30 Si₁₉Co₁₃Co₂O₄N₀₉O₆⁰</td>
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<tr>
<td>Co/SiN500</td>
<td>57.40 22.32 0.93 16.36</td>
<td>2.99 Si₁₉Co₁₃Co₂O₄N₀₉O₆⁰</td>
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<tr>
<td>Co/SiN800</td>
<td>52.89 16.70 0.50 23.73</td>
<td>6.18 Si₁₉Co₁₃Co₂O₄N₀₉O₂¹</td>
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<tr>
<td>Co/SiN1000</td>
<td>53.84 16.08 0.01 26.99</td>
<td>3.98 Si₁₉Co₁₃Co₂O₄N₀₉O₂¹</td>
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Fig. 1 XRD patterns of Co/SiNX samples.

Fig. 2 TG–MS analyses under flowing He of the Co-PHPS sample: (a) a TG-curve and a total ion current chromatogram, (b–e) the simultaneous monitoring of gaseous products formed in situ.
As shown in Fig. S1 (ESI†), a color change from blue to gray was observed for the CoCl₂-dispersed PHPS solution after reflux at 110 °C for 12 h. The visible color change was also monitored by UV-Vis absorption spectroscopy (Fig. S2, ESI†): as-received CoCl₂ exhibits a broad peak around 600 nm attributed to octahedral coordination of CoCl₂, while the Co-PHPS sample recovered after the 110 °C-refluxing in toluene presents additional absorption bands at 670 and 700 nm assigned to typical bands of tetrahedral coordination which were attributed to the formation of CoCl₃L₂ (L = ligands). In addition, according to the FTIR spectrum of the Co-PHPS shown in Fig. 3, the characteristic bands at 3370 cm⁻¹ (nN–H) of PHPS slightly shift toward lower wavenumber of 3365 cm⁻¹, suggesting the CoCl₂ coordination to the NH group of PHPS during the precursor synthesis. We therefore suggest that the reaction between PHPS and CoCl₂ better proceeded during the pyrolysis, and the NH₄Cl species detected in the XRD patterns of the Co/SiN₄00 and Co/SiN₅00 samples (Fig. 1) are by-products resulting from the nucleation reaction between HCl formed in situ and the gaseous NH₃. As shown in Table 1, the Co/Si ratio of the Co/SiN₄00 sample (0.37) was apparently higher than the nominal Co/Si ratio of Co-PHPS (0.2), which can be explained by the elimination of chlorosilanes at 220–350 °C (Fig. 2(d) and (e)), i.e., the number of SiH groups decreases. Furthermore, from 400 to 500 °C, the N/Si atomic ratio decreased from 0.75 to 0.57 (Co/SiN₅00). This corresponds to the reported thermal decom- position of Co₃N at 350–450 °C. Consequently, these results indicate that the following reactions proceed stepwise:

(i) At 220–350 °C, Si–N cleavages in the Co-PHPS sample proceed via reaction of the Si center and NH group of PHPS with CoCl₂ associated with the elimination of chlorosilanes and HCl to afford Co₃N, respectively.

(ii) At 350–450 °C, Co₃N thermally decomposes to yield metallic-Co.

The N/Si ratio of the Co/SiNX samples in Table 1 increased during pyrolysis from 500 to 1000 °C, indicating the occurrence of nitridation of the evaporated polymer under ammonia above 500 °C. Moreover, the crystallization of Si₃N₄ started at 800 °C, which was approximately 400 °C lower than that of Co-free PHPS-derived amorphous silicon nitride. Table 2 presents the relationship between the pyrolysis temperature and the average crystallite sizes evaluated for a-Co(101) and b-Co(111). The initial low-temperature crystallization (400 °C) of a-Co yields crystallites of approximately 106 nm. Then, consistent with the pyrolysis temperature, the a-Co nanocrystallites decrease their size via phase transformation to thermally favorable b-Co, and the Scherrer analysis indicated an average b-Co nanocrystallite size of 74.4 nm for the Co/SiN₈00 sample.

To gather micro- and nanostructural information, TEM investigations were performed on the Co/SiN₈00 sample (Fig. 4). The TEM image of the Co/SiN₈00 sample (Fig. 4) shows aggregated nanocrystallites with dark contrast and diameter of about 40–80 nm which are embedded in a network with the typical phase contrast of amorphous (or poorly crystallized) materials. The corresponding selected area electron diffraction (SAED) patterns confirm the indexation of both a- and b-Co (inset in Fig. 4). Neither silicon segregations nor inclusions along grain boundaries are observed, while dark spots with several nanometers in size (typical ones are indicated by arrows) are observed which suggested that the crystallite size distribution of Co embedded within the silicon nitride matrix is bimodal: several nanometers and 40 to 80 nm.

In conclusion, the addition of cobalt chloride (CoCl₂) on perhydropolysilazane (PHPS) in toluene in a 1/5 molar ratio generated a cobalt-coordinated PHPS that was heat-treated in flowing ammonia in the temperature range of 400 to 800 °C to favor the in situ growth of Co nanoparticles in an amorphous silicon nitride matrix. The highlights can be summarized as follows:

1. Formation of Co₃N in situ by the reaction of CoCl₂ with the Si center and NH group of PHPS at 220–350 °C.
2. Co started growing at temperature as low as 400 °C via the thermal decomposition of Co₃N.
3. Crystallization of the amorphous silicon nitride matrix proceeded at 800 °C.

Further investigations on the molecular structure of the single-source precursors and subsequent pyrolysis conditions at the low temperatures are still in progress. Therefore, this study paves the way for the rational one-step synthesis of metal/nitride nanocomposites that may be applied in a wide range of catalysis-assisted reactions for energy-related fields. These opportunities are now being addressed. It is anticipated that

<table>
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<th>Table 2 Relationship between the pyrolysis temperature and the average crystallite sizes evaluated for a-Co(101) and b-Co(111)</th>
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<tr>
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<td>a-Co(101)</td>
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<td>b-Co(111)</td>
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this will lead to a host of structural and functional applications for a new generation of advanced ceramics.

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Notes and references