Magnetic Fe–Co and Its Oxide Nanopowders
Produced by Chemical Vapor Condensation

Jin-Chun Kim¹*, Chul-Jin Choi¹, Jae-Wook Lee, Z. H. Wang² and Z. D. Zhang²

¹Korea Institute of Machinery and Materials, 66 Sangnam-Dong, Changwon Kyungnam 641-831, Korea
²Shenyang National Laboratory for Materials Science Institute of Metal Research Academia Sinica, Wenhua Road 72 Shenyang, 110016, People’s R. O. China

Fe–Co magnetic nanopowders were prepared by chemical vapor condensation (CVC) process, and some of their characteristics such as phase, size, oxidation behavior, and magnetic properties were investigated. Thermal behaviors of Fe–Co nanopowders were also studied by means of annealing in the air. Iron pentacarbonyl (Fe(CO)₅) and dicobalt octacarbonyl (Co₂(CO)₈) were used as precursors. XRD patterns showed that Fe–Co nanopowders were obtained in pure Ar, but that the Fe and Co oxide nanopowders were produced in the Ar + O₂ mixtures. Fe–Co nanopowders obtained in pure Ar consist of a core and a shell with a thickness of 2–4 nm. The saturation magnetization and coercivity decreased with increasing oxygen content in the carrier gases. The CVC nanopowders obtained in different carrier gases showed different Mössbauer spectrums.

(Received May 6, 2005; Accepted July 7, 2005; Published September 15, 2005)

Keywords: chemical vapor condensation, nanopowder synthesis, oxidation, iron-cobalt nanopowder, magnetic property, thermal stability

1. Introduction

Nanopowders of various materials have been intensively studied for both fundamental understanding of their physical/chemical properties and their applications in various fields because their properties are different from those of bulk materials.¹⁻⁵ Just like other materials, magnetic nanopowders have also been studied because of their special characteristics such as single-domain magnetism and superparamagnetism, when their size is less than that of magnetic single domain. The difference in magnetization and coercivity of magnetic nanopowders has resulted from a presence of nonmagnetic oxide surface and a canting in the oxides coating.⁶

Nanostructured powders have been fabricated through various routes; CVC process is one of the most attractive methods because a wide variety of metal-organic precursors are available.⁷⁻⁹ Final characteristics of CVC powders are intensively dependent on the parameters of preparation conditions such as decomposition temperature of precursors, the reaction temperature, and kinds of carrier gases. However, one of the most important factors is how to prevent oxidation during the synthesis of nanopowders, because nanopowders are very reactive in the air, and such problems become more serious when the particle size is quite small with a very large surface area. For prevention of oxidations, one of the motivations of this work is to investigate the oxidation behavior and understand the oxidation process of CVC nanopowders.

In this work, Fe–Co magnetic nanopowders were produced by the CVC method with Fe(CO)₅ and Co₂(CO)₈ under different carrier gases, i.e., Ar and Ar + O₂ mixture. Microstructure, oxidation behavior, thermal stability, and magnetic characteristics of nanopowders are studied under different conditions.

*Corresponding author, E-mail: jckimpml@kmail.kimm.re.kr

2. Experimental Details

The basic setup of CVC process in this work was similar to that described elsewhere in the literature.¹⁰ To synthesize Fe–Co nanopowders, two organometallic compounds, Fe(CO)₅ and Co₂(CO)₈, were used as precursors. The former was a liquid with a boiling temperature of 103°C, which can be easily transported into bubbler by a micro-pump at room temperature, but the latter was a solid crystalline powder with a melting point of 51°C. Therefore, two bubblers were used to vaporize the precursors.

Nanopowders were synthesized with different carrier gases such as pure Ar, Ar + 1%O₂, Ar + 3%O₂ and Ar + 6%O₂ using high purity Ar(99.999%) and Oxygen(99.99%). The total flow rate of the carrier gas was fixed as 400 cm³/s. The carrier gas was fed through heated bubblers containing the precursors. Two precursors’ vapors were mixed with the carrier gas before entering the heated furnace. They were decomposed and reacted in the tubular furnace, which was made of a high purity alumina tube. The length of the reaction zone of the furnace was about 7 cm. The temperature of the reaction furnace was kept at 700°C. The precursor vapors were condensed into nanopowders on the rotating chiller, which was cooled by liquid nitrogen in the collection chamber. Finally, the powders were stripped off from the chiller and stored.

Phase structures identification of the nanopowders was carried out by X-ray diffraction (XRD) with CuKα radiation. Morphologies were determined using a transmission electron microscopy (TEM). The average size of CVC powder was determined by Brunauer–Emmett–Teller (BET) specific surface and TEM images. The composition of powders was determined by induction coupled plasma (ICP) spectroscopy. The oxygen content of the CVC powders was determined on an O/N analyzer (Eltra ON 900). Magnetic measurements at room temperature were carried out by the vibrating sample magnetometer (VSM) in the fields up to 1591.55 kA/m. Mössbauer absorption spectra were recorded on a conven-
tional constant acceleration spectrometer using a $^{57}$Fe source at room temperature. The thermal and oxidation behaviors were investigated by means of annealing treatment at 580°C, 680°C and 840°C in the air with a heating rate of 10°C/min.

3. Results and Discussions

Figure 1 shows the XRD patterns of the as-prepared powders obtained with different carrier gases at 700°C. In the pure Ar, the single-phase powders were obtained as shown in Fig. 1(a). According to the analysis of XRD patterns, the nanopowders produced in this condition are the Fe–Co alloy phase. But as the content of the oxygen in the argon increased, the peaks corresponding to the oxides of the iron and cobalt were much more abundantly observed. In the Ar $+$ 1%O$_2$ gas, the as-prepared powders had Fe–Co and its oxide phase, which is partially oxidized. When the oxygen content was over 3%, only the peaks of the iron oxides (Fe$_2$O$_3$ or Fe$_3$O$_4$) and cobalt oxide (CoO) were present. It suggests that all iron and cobalt were easily oxidized in this process. As the oxygen content in the carrier gas was increased, the peaks broadened indicating that the size of CVC powders became smaller because the oxidation mechanism was different from the carrier gases (see Fig. 3).

The characteristics of CVC Fe–Co nanopowders prepared by changing the carrier gases are summarized in Table 1. The oxygen contents are different for all samples. The average powder size decreased with increasing oxygen content of carrier gases as mentioned in the XRD results. The average powder size decreased from 16.2 to 10.3 nm when 1% oxygen is mixed in the Ar. The oxygen content of the as-prepared powders enhanced with increasing oxygen content in the carrier gas. The colors of the powders changed from black to brown when the oxygen content increased from 0% to 6%, corresponding to the formation of the iron oxides.

Figure 2 shows the TEM microstructure of CVC Fe–Co nanopowder obtained in the different carrier gases, (a) Ar and (b) Ar $+$ 6%O$_2$. The powder obtained in the Ar appeared nearly spherical with a core-shell structure because the surface of the powder was oxidized during the passivation process. The thickness of the

![Fig. 1](image1.png) XRD patterns of the CVC nanopowders prepared at 700°C in the different carrier gases; (a) pure Ar, (b) Ar $+$ 1%O$_2$, (c) Ar $+$ 3%O$_2$ and (d) Ar $+$ 6%O$_2$.

![Fig. 2](image2.png) TEM micrograph of the CVC Fe–Co and its oxide nanopowder obtained in the different carrier gases, (a) Ar and (b) Ar $+$ 6%O$_2$.

<table>
<thead>
<tr>
<th>Carrier gas (sccm)</th>
<th>Size (nm)</th>
<th>O content (mass%)</th>
<th>As-prepared powder’s color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>16.2</td>
<td>19.52</td>
<td>black</td>
</tr>
<tr>
<td>Ar $+$ 1%O</td>
<td>10.3</td>
<td>29.26</td>
<td>bright brown</td>
</tr>
<tr>
<td>Ar $+$ 3%O</td>
<td>6.13</td>
<td>33.93</td>
<td>brown</td>
</tr>
<tr>
<td>Ar $+$ 6%O</td>
<td>6.40</td>
<td>33.87</td>
<td>brown</td>
</tr>
</tbody>
</table>

Table 1 Effect of carrier gases to the properties of the nanoparticles.
shell is about 2–4 nm. However, the powder produced in the 
Ar + 6%O₂ did not have the core-shell structure because it 
was fully oxidized under this condition. Even though the 
powders were oxidized, all the powders had a narrow size 
distribution and were connected to chains because of their 
magnetism and high specific surface area.

It was reported that Fe(CO)₅ is decomposed to Fe + 5CO 
in the temperature range of 160–200 °C, and Co₂(CO)₈ is 
pyrolyzed to 2Co + 8(CO) in the temperature range of 80– 
90 °C. Therefore, during CVC process, the formation 
procedure of the Fe–Co and its oxide powders in CVC 
process could be explained schematically in Fig. 3. In the 
pure Ar atmosphere, Fe and Co vapor decomposed from their 
precursors were mixed before coming into the reaction 
furnace, and they reacted each other into the metallic Fe–Co 
alloy clusters. And in the reaction furnace, the metallic Fe– 
Co clusters actively coagulated and formed into pure metallic 
Fe–Co nanopowders. Finally, when Fe–Co nanopowders 
were collected from the chamber in the air, they were 
oxidized, and the oxide shell of Fe–Co nanopowders was 
formed. On the other hand, in the oxidation atmosphere of 
Ar + O₂ carrier gases, each metallic Fe and Co vapor 
actively reacted with oxygen, and then transformed into their 
oxide nanopowders. Generally, the coagulation or growth of 
the oxide powders was more difficult the metallic Fe–Co 
state. Thus, the size of the Fe and Co oxide powders would be 
smaller than that of the metallic Fe–Co state. Therefore, the 
oxidation reaction did not progress further during the 
passivation process in the air, and the different iron and 
cobalt oxides (Fe₂O₃, Fe₃O₄ and CoO) nanopowders were 
produced as shown in XRD patterns.

The magnetic properties of the powders are shown in 
Fig. 4. When the oxygen content in the carrier gas was 
increased, the saturation magnetization and coercivity de-
creased dramatically from 11.56 × 10⁻⁵ Wb-m/kg and 
62.87 kA/m to 1.26 × 10⁻⁵ Wb-m/kg and 12.73 kA/m, 
respectively. The biggest particle sample was obtained in 
pure Ar without the appearance of the oxides during the 
synthesis process, and thus it has the largest values of 
magnetization and coercivity. As the carrier gas was mixed 
with the oxygen, the oxides were synthesized during the 
process, while the particle size became small, and conse-
quently the magnetization and coercivity decreased. When the oxygen content was larger than 3% in the carrier 
gas, the changes in saturation magnetization and coercivity 
became less progressed.

Mössbauer spectra at room temperature of the sample (a) obtained in pure Ar and the sample (b) obtained in Ar + 3% O are illustrated in Fig. 5. Table 2 shows the fitting results of
Mössbauer spectra of the two samples. Analyzing the fitting results of Mössbauer spectra, we found that it is possible that some moisture absorption may occur in particles to form α-FeOOH during/after the passivation process. As shown in Fig. 5(a), Mössbauer spectrum of the Fe–Co nanopowders prepared in Ar atmosphere consist of six-line sub-spectrum, showing an evidence of ferromagnetism. The areas for ferromagnetic and paramagnetic phases are 83 and 17%, respectively. The paramagnetism could arise from the superparamagnetism of the part of Fe–Co powders with very small particle size, although the average particle size is slightly bigger than 10 nm showing the superparamagnetism. We think that α-FeOOH cannot show superparamagnetism because its particle size is distributed over a wide range from bulk to middle. Mössbauer spectrum of the oxide nanopowder [Fig. 5(b)] has a strong doublet peak, showing the existence of the paramagnetism. It is clear that the paramagnetism is arisen from superparamagnetism, because of its small average particle size of 6.13 nm. As to the presence (7%) of middle α-FeOOH with fine particle size, it is quite possible that there exist fine Fe–Co particles showing superparamagnetism. An XRD analysis shows that there are only Fe–Co peaks for sample (a), coinciding with Mössbauer results, and other phases were not detected from XRD because the particle size is very small. The particle size is generally very small from line broadening of peaks in XRD analysis of sample (b), which coincides exactly with Mössbauer analysis.

In order to investigate the thermal stability, the CVC powders produced in Ar (a) and Ar + 6%O2 (b) were heat-treated at different temperatures. The XRD patterns of the heat-treated nanopowders are shown in Fig. 6. The reactions before 500 °C were similar to previous work.7,8 In the sample (a), the peaks of β-Fe2O3, Co3O4 and CoFe2O4 appeared at 580 and 680 °C, and their amounts were enhanced by increasing the temperature from 580 to 840 °C. When the Fe–Co nanopowders prepared in Ar were heated in the air, the oxidation, the phase change, and the particle growth all occurred simultaneously. Therefore, the oxides such as Co3O4, Fe2O3 and CoFe2O4 were formed. The peak intensity and the width were increased and narrowed because of the particle growth of the CVC powders. On the other hand, the oxide nanopowders obtained in the Ar + 6%O2 were relatively stable compared to the metallic Fe–Co nanopowders. Therefore, when the sample (b) was treated at 580°C, there were no evident changes from the as-prepared CVC powders. However, at 680°C, the unstable oxides were transformed into stable oxides such as CoFe2O4 and Co3O4 as shown in Fig. 6(b).

### Table 2 Results of Mössbauer spectroscopy analysis for sample(a) and sample (b).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Core (%): Bulk</th>
<th>Core (%): Middle</th>
<th>Shell: α-FeOOH (%): Bulk</th>
<th>Shell: α-FeOOH (%): Middle</th>
<th>Super-Magnetism (%): Bulk</th>
<th>Super-Magnetism (%): Middle</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>37</td>
<td>0</td>
<td>6</td>
<td>18</td>
<td>22</td>
<td>17</td>
<td>16.2</td>
</tr>
<tr>
<td>b</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>7</td>
<td>0</td>
<td>93</td>
<td>6.13</td>
</tr>
</tbody>
</table>

Fig. 6 XRD patterns of the CVC nanopowders produced in the (a) Ar and (b) Ar + 6%O2 and the their heat-treated CVC nanopowders at different temperature in air.

4. Conclusions

Fe–Co Nanopowders and their oxides have been synthesized by CVC, using pure Ar, Ar + 1%O2, Ar + 3%O2 and Ar + 6%O2 as carrier gases. The color of the as-prepared nanoparticles changes from black to brown, corresponding to the formation of the iron oxides. The average powder size decreased from 16.2 to 6.13 nm with increasing oxygen content because the Fe–Co nanopowder formation and
oxidation mechanism were different from the carrier gases. The saturation magnetization and coercivity decreased with increasing oxygen content in the carrier gases because of the decrease of the volume fraction of pure magnetic Fe–Co phase, the average powder size, and the appearance of the oxides. Mössbauer spectrum of the Fe–Co nanopowders prepared in Ar atmosphere were ferromagnetic, but the Fe–Co oxide powders showed the presence of paramagnetism. Heat treatment in the air resulted in the appearance of stable oxide phases such as \( \beta\text{-Fe}_2\text{O}_3 \), \( \text{CoFe}_2\text{O}_4 \), and \( \text{Co}_3\text{O}_4 \). The CVC powders obtained in different carrier gases showed different thermal behaviors.

Acknowledgements

The authors would like to sincerely thank a senior researcher Dr. Jae-Wook Lee of Korea Institute of Machinery and Materials for his many comments for analyzing the magnetic properties.

REFERENCES