Application of Nanostructured powders synthesized by new chemical processes

2003. 10
Byoung-Kee Kim

Korea Institute of Machinery and Materials,

Characteristics of Nanopowder Materials

<table>
<thead>
<tr>
<th>Property</th>
<th>Materials</th>
<th>Size (Å)</th>
<th>Nanomaterials</th>
<th>Micro-materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic Property</td>
<td>Fe</td>
<td>50</td>
<td>1030Oe</td>
<td>~470Oe</td>
</tr>
<tr>
<td>Melting Point</td>
<td>Au, In</td>
<td>30, 40</td>
<td>933K, 370K</td>
<td>1300K, 430K</td>
</tr>
<tr>
<td>Light Absorption (6–10Å)</td>
<td>Au</td>
<td>100</td>
<td>95%</td>
<td>2–5%</td>
</tr>
<tr>
<td>Transition Temperature of Superconductivity</td>
<td>Al</td>
<td>90</td>
<td>5.3K</td>
<td>3.4K</td>
</tr>
<tr>
<td>Heat Transfer</td>
<td>Ag</td>
<td>100</td>
<td>2.0mK</td>
<td>20mK</td>
</tr>
<tr>
<td>Sintering Temperature</td>
<td>Ni, W</td>
<td>200, 220</td>
<td>~200°C ~1000°C</td>
<td>760°C</td>
</tr>
<tr>
<td>Catalytic Property (As - standard Activity)</td>
<td>Ni</td>
<td>10</td>
<td>6As</td>
<td>~3As</td>
</tr>
</tbody>
</table>

Surface Effect
- Enhanced catalytic properties
- Enhanced absorption ability
- Capillary Condensation

Bulk Effect
- Appearance of New Phases
- Decrease of Melting Point
- Polycrystallization of Single Crystal
- Enhanced Scattering Effect of Waves

Interaction between Nanopowders
- Electric and heat transfer
- Compressibility
- Solid state reactivity
Application Field of Nanopowder Materials

Electronic
- Optoelectronic devices
- Passive electronic devices
- IC substrate
- Thermistor and varistor
- Piezoelectric actuators
- CMP

Optical

Magnetic
- Advanced tones
- Diagnostic contrast agents
- Ferrofluids
- Magnetic Recording
- Magnetic Refrigerator

Structural
- Cutting tool
- Die
- Coating
- Abrasive components

Others
- Catalysts
- Chemical sensors
- Energy storage devices
- Pigments
- Membranes

Research of Nanopowders in KIMM

<table>
<thead>
<tr>
<th>Area</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tool Materials</td>
<td>Abrasives, Cutting tools, CMP, Wear-resistant components</td>
</tr>
<tr>
<td></td>
<td><em>WC-Co hard materials</em></td>
</tr>
<tr>
<td>Magnetic Materials</td>
<td>Ferrofluid, Magnetic refrigerator, Recording media,</td>
</tr>
<tr>
<td></td>
<td>Hard/Soft Magnets, <em>Fe/Co magnetic materials</em>,</td>
</tr>
<tr>
<td></td>
<td><em>Nd-Fe-B hard magnet</em></td>
</tr>
<tr>
<td>Electric/Electrode Materials</td>
<td>Thermistor, Varistor, Piezoelectric actuator</td>
</tr>
<tr>
<td></td>
<td><em>Cu-Al₂O₃ electrode, W-Cu heat sink</em></td>
</tr>
<tr>
<td>Chemical/Catalytic Materials</td>
<td>Chemical Sensor, Membranes, Filter, <em>TiO₂ photocatalysts</em></td>
</tr>
</tbody>
</table>
Mechanical Properties of WC/Co

- Chemical compositions (contents of Co)
- Particle size of hard phase (WC)
- Homogeneity of WC/Co (mean free path)

Reduction of WC size
- Decrease of mean free path

Key for high mechanical properties
- Fabrication of very fine WC
- Higher homogeneity of WC and Co phases

Manufacturing of WC/Co Alloys

**Solid Phase Process**
- APT powder
- Calcinations
- Milling (+C)
- Reduction
- Milling (+Co)
- Carburization
- G.S. > 300nm

**Liquid Phase Process**
- W, Co chlorides
- Spray drying
- Removal of Chlorides
- Reduction / Carburization
- Milling (+C)
- G.S. > 100nm

**Gas Phase Process**
- W, Co metalorganics
- Evaporation / Carburization
- WC, WC + Co
- G.S. < 30nm

KIMM
Korea Institute of Machinery and Materials
**n- WC powder**

- WC
- W/C
- W2(CO)
- W
- He
- H2/He
- H2/CH4
- Total: 600sccm

- Low pressure (10^-3 atm)
- Size: 5nm

**Coating of n- WC, Co powder**

- Carbon coating WC powder
- Oxide coating Co, Fe powder

- WC powder: 4nm
- Core(metal)/Shell(Oxide)
- Oxide shell: 3nm

- Weight Change (%)
- Temperature (°C)

KIMM Korea Institute of Machinery and Materials
Compactability of n-WC powder

<table>
<thead>
<tr>
<th>Type</th>
<th>Power size</th>
<th>BET (m²/g)</th>
<th>A.D. (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>20nm</td>
<td>18.4</td>
<td>0.77</td>
</tr>
<tr>
<td>B</td>
<td>100nm (granule)</td>
<td>2.02</td>
<td>1.85</td>
</tr>
<tr>
<td>C</td>
<td>100nm</td>
<td>3.09</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Compact density 47%

Sinterability of n-WC/Co powder

Solid sintering temp.
- WC(20nm)+Co(20nm) : 835°C
- WC(20nm)+Co(100nm) : 890°C
- WC/Co(100nm) : 1010°C
- WC/Co(200nm) : 1070°C

- sintering temp: WC size(1070-835°C)
- Co size (890-835°C)
- abnormal grain growth (100 times)

Grain growth inhibitors
Plasma sintering/grain growth inhibitor

Plasma sintering

Conventional WC-10Co

- High Dislocation Density
- Stacking Faults

WC-10Co

facetted shape 1

(x 50)

Nano. WC-10Co

- Dislocation free WC grains
- Twins in WC grains

WC-10Co-0.6VC

round, 70nm (x 4)

Properties of Nanostructured WC-Co Alloy

<table>
<thead>
<tr>
<th>Property</th>
<th>TCP</th>
<th>MCP</th>
<th>Submicron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness (Hv)</td>
<td>2550</td>
<td>1950</td>
<td>350</td>
</tr>
<tr>
<td>TRS (kgf/mm²)</td>
<td>1650</td>
<td>200</td>
<td>1.2E-9</td>
</tr>
<tr>
<td>Wear rate (mm³/m)</td>
<td>2.1E-9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

KIMM Korea Institute of Machinery and Materials
Nano sized Fe and Co Magnetic Materials

- Magnetic Fluid: Magnetite (Fe₃O₄)
- Saturation Magnetization of Fe = 2 times of that of Fe₃O₄
  Coercivity: proportional to inverse of particle size (Hc = a+b/D)
- Synthesis of nano-sized Fe ⇒ High performance magnetic fluid materials (Saturation Magnetization: 1500emu/cm³, Coercivity: 3000Oe)

Development of Fe based nanopowder for magnetic fluids by Chemical Vapor Condensation

Microstructures of Fe Nanoparticles

- Core: Crystalline Fe
- Shell: Crystalline Fe oxides

Intensity (arb. unit)

5 nm
**Mössbauer spectroscopy of Fe nanoparticles**

<table>
<thead>
<tr>
<th>Samples</th>
<th>α-Fe (%)</th>
<th>Superparamagnetism (%)</th>
<th>Fe3O4 (%)</th>
<th>Mean size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>2</td>
<td>0</td>
<td>98</td>
<td>0.39</td>
</tr>
<tr>
<td>(b)</td>
<td>20</td>
<td>5</td>
<td>75</td>
<td>0</td>
</tr>
<tr>
<td>(c)</td>
<td>34</td>
<td>21</td>
<td>21</td>
<td>10.32</td>
</tr>
<tr>
<td>(d)</td>
<td>70</td>
<td>0</td>
<td>0</td>
<td>-120</td>
</tr>
</tbody>
</table>

**Microstructures of Fe-Co nanoparticles**
**Phases of Co nanoparticles with carrier gases**

Carrier gas: Ar

Carrier gas: Ar + 6%O₂

Carrier gas: He

Carrier gas: BCC Co + HCP Co

Carrier gas: BCC Co

Carrier gas: Co oxide

**Phases and saturation magnetization**

Different phases with different Co content

Saturation magnetization reaches highest value near 40 wt% Co
Nanostructured TiO₂ photocatalytic materials

- Decrease of particle size
  - Improved UV scattering
  - Enhanced photocatalytic activity
  - Improved gas sensing property
  - Enhanced opto-electronic property

- Synthesis of nano sized TiO₂ powders by Chemical Vapor Condensation process (Non-Agglomerated 10nm powder)

Microstructure of Nano-sized TiO₂ Powder

- size: 10nm
- loose agglomerates
- phases: Anatase + Rutile (<2%)
Phase Change Depending on Powder Size

Anatase
\[a = 3.75 \text{Å}, c = 9.51 \text{Å}\]

Rutile
\[\sim 60 \text{nm}\]

[100] zone axis
(110) type planes

Nanostructured W-Cu heat sink materials

- Poor sinterability due to the negligible solid solubility between W and Cu
- Conventional Process
  - Infiltration: Low thermal & electric conductivity due to the addition of sintering activator
  - Liquid phase sintering: Low properties due to larger W size
- Development of new process to achieve high density nanostructured W/Cu materials, using nanostructured powder (W : 60nm)
Microstructures of W/Cu Alloys

Mixing method
W:0.51%, Cu:20%

Thermochemical method
(W-20wt%+0.5wt%Co)

Mechano-thermochemical method(I)
Burnt out powder, Two-reduction step

Mechano-thermochemical method(II)
Reduced powder (200°C/1h+700°C/1h)

KIMM
Korea Institute of Machinery and Materials

Sinterability of Nanostructured W/Cu Powders

Sintering density
- Burnt out powder (process I)
- Reduced powder (process II)
- Metal mixed powder

Green density
- Burnt out powder
- Reduced powder
- Metal mixed powder

Cu melting point

Relative density (%) vs. Sintering temperature (°C)
Comparison of Thermal Properties

<table>
<thead>
<tr>
<th></th>
<th>W-20Cu Thermkom -76</th>
<th>W-20Cu Thermkom -83</th>
<th>Mo-15Cu Thermkom -65M</th>
<th>Mo-20Cu Thermkom -70M</th>
<th>W-20Cu KIMM 700-8</th>
<th>W-20Cu KIMM 700-8</th>
<th>W-20Cu KIMM 750-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>15.94</td>
<td>14.63</td>
<td>9.89</td>
<td>9.81</td>
<td>15.48-L</td>
<td>15.43-L</td>
<td>15.16-L</td>
</tr>
<tr>
<td>Specific Heat (J/Kg K)</td>
<td>223.2</td>
<td>240.1</td>
<td>294.5</td>
<td>300.0</td>
<td>223.2</td>
<td>223.2</td>
<td>223.2</td>
</tr>
<tr>
<td>Thermal Conductivity (W/mK)</td>
<td>207 (180-210)</td>
<td>242 (180-210)</td>
<td>141 (180-210)</td>
<td>170 (180-210)</td>
<td>233.0</td>
<td>245.8</td>
<td>221.3</td>
</tr>
<tr>
<td>Thermal Expansion Coefficient (ppm/K)</td>
<td>6.5 (7.2-8.0)</td>
<td>8.0 (8.1-8.9)</td>
<td>5.4 (6.0-7.0)</td>
<td>6.5 (6.8-7.6)</td>
<td>7.80</td>
<td>7.80</td>
<td>7.25</td>
</tr>
</tbody>
</table>

Prospect of Nanopowder Materials

- **Ceramics**
  - Electro-optical Device and Ferroelectrics
  - Thin Films
  - Superhard Materials

- **Cermet**
  - Drilling, Mining and Machine Tools

- **Metals**
  - Transportation Energy, Chemical Industries
  - Protective Coatings
  - Advanced Nanocomposites
  - Energy And Aerospace Industries

Years: 5, 10, 15