4.5.4 Pulsed Laser Method

Silver nitrate + reducing agent $\rightarrow$ Silver nanoparticle

Figure 4.28. Apparatus to make silver nanoparticles using a pulsed laser beam that creates hot spots on the surface of a rotating disk. [Adapted from J. Singh, Mater. Today 2, 10 (2001).]
Laser Ablation
Laser Ablation
1. Quantum size effects on the competition between Kondo interaction and magnetic order in 0-D.

Conclusion:
In 80A -CeAl₂, magnetic ordering completely disappears and the γ reaches 9500 mJ/mol Ce K².

Unsolved problems:
In nanoparticle, only 0.7 Mole Ce ³⁺ left, Is the 0.3 mol non-magnetic Ce really on the surface ? or it is just a coincidence.
4.6 Conclusion

In this chapter a number of examples have been presented showing that the physical, chemical, and electronic properties of nanoparticles depend strongly on the number and kind of atoms that make up the particle. We have seen that color, reactivity, stability, and magnetic behavior all depend on particle size. In some instances entirely new behavior not seen in the bulk has been observed such as magnetism in clusters that are constituted from nonmagnetic atoms. Besides providing new
Chapter 6 Bulk Nanostructured Materials

• Bulk nanostructured materials are solid
• having
• 1. a nanosized microstructure
• 2. the basic units are nanoparticles
Disordered Al$_{12}$ Particles

Figure 6.1. (a) Illustration of a hypothetical two-dimensional square lattice of Al$_{12}$ particles, and (b) illustration of a two-dimensional bulk solid of Al$_{12}$ where the nanoparticles have no ordered arrangement with respect to each other.
6.1 Solid disordered nanostructure

- Compaction and consolidation
- 1. 85%Cu and 15%Fe powder in atomic weight
- 2. Ball milling to form Fe$_{85}$Cu$_{15}$ particles
- 3. Compacted using a tungsten-carbide at 1GPa
- 4. Hot compaction at ~ 400°C with 870 MPa
- Density 99.2%
Figure 6.2. Distribution of sizes of Fe–Cu nanoparticles made by hot compaction methods described in the text. [Adapted from L. He and E. Ma, J. Mater. Res. 15, 904 (2000).]
CeAl$_2$ HRTEM
Fracture stress enhanced from 0.56 GPa (40 nm grain) to 2.8 GPa (50-150 um grain Iron)

Ductile region

Young’s modulus

Ductile? 柔軟
Brittle? 脆
Rapid solidification-Chill block melt spinning

Figure 6.4. Illustration of the chill block melting apparatus for producing nanostructured materials by rapid solidification on a rotating wheel. (With permission from I. Chang, in Handbook of Nanostructured Materials and Nanotechnology, H. S. Nalwa, ed., Academic Press, San Diego, 2000, Vol. 1, Chapter 11, p. 501.)
Light weight, high strength materials

1. A melt spun alloy Al(85-94\%)\text{-}Y\text{-}Ni\text{-}Fe
2. Consisting of 10\text{-}30 \text{ nm} Al particles
3. Tensile strength $\sim$1.2 GPa
Gas atomization

Figure 6.5. Illustration of apparatus for making droplets of metal nanoparticles by gas atomization. (With permission from I. Chang, in Handbook of Nanostructured Materials and Nanotechnology, H. S. Nalwa, ed., Academic Press, San Diego, 2000, Vol. 1, Chapter 11, p. 501.)
Electrodeposition (P137)

- Electrodes
- Electrolyte (電解液)
- Cu 2 mm film with grain size of 27 nm
- Enhanced yield strength 119 MPa
6.1.2 Failure mechanisms of conventional grain-sized materials

Crack!

An irreversible elongation after breaking of the bond

Figure 6.6. A crack in a two-dimensional rectangular lattice.
Brittle to ductile transition

1. Lattice slide
2. Weaker bonds along the dislocation

B to D region

Lattice dislocation.

Hardening: to Impede the movement of dislocation by introducing tiny particles iron carbide

Figure 6.7. An edge dislocation in a two-dimensional rectangular lattice.
6.1.3 Mechanical Properties

• 1. Young’s modulus: stress-strain ratio
• 2. The yield strength \( s \) is described by
  - Hall-Petch equation for a conventional grain-size materials
  - \( s = s_0 + K/d^{0.5} \)
  - Materials having smaller grains have more grain boundaries, blocking dislocation movement
• 3. Bulk nanostructured materials are quite brittle and display reduced ductility (~ a few % elongations) for grain size < 30 nm. Due to flaws and porosity
6.1.4 Nanostructured multilayers

Due to Increasing interfaces and structure mismatch
6.1.5 Electrical properties

Figure 6.12. Cross-sectional view of a lithographically fabricated device to measure the electrical conductivity in a two-dimensional array of gold nanoparticles linked by molecules. (With permission from R. P. Andres et al., in *Handbook of Nanostructured Materials and Nanotechnology*, H. S. Nalwa, ed., Academic Press, San Diego, 2000, Vol. 3, Chapter 4, p. 217.)
\[ G = G_0 \exp\left(\frac{-E}{k_B T}\right) \]

E: activation energy

Room-temperature current–voltage relationship for a two-dimensional cage (line a) and with the particles linked by a (CN)₂C₁₈H₁₂ molecule (line b). (James et al., Supercell Microstruk 18, 875 (1995)).
Electron tunneling

Figure 6.15. Sketch of a model to explain the electrical conductivity in an ideal hexagonal array of single-crystal gold clusters with uniform intercluster resistive linkage provided by resistors.
The no. of electrons that can move Net Current

\[ N_1(E - eV)f(E - eV)[N_2(E)(1 - f(E))] \]  \hspace{1cm} (6.3)

\[ I = K \int N_1(E - eV)N_2(E)[f(E - eV) - f(E)]dE \]  \hspace{1cm} (6.4)

\[ G_{nm} = KN_1(E_f)N_2(E_f)e \]  \hspace{1cm} (6.7)
6.1.8 Porous Silicon made by electrochemical etching in hydrogen fluoride

Luminescence: Absorption of energy
Reemit Visible or near-visible light

Fluorescence: emission occurs within $10^{-8}$ s

Phosphorescence: a delay emission

Luminescence spectra of porous silicon for two different exposure times. Note the change in scale for the two curves. (Adapted from Xie et al.)
p-type silicon is etched, a very fine network of pores having dimensions less than 10 nm is produced.

A number of explanations have been offered to explain the origin of the fluorescence of porous silicon, such as the presence of oxides on the surface of the pores that emit molecular fluorescence, surface defect states, quantum wires, quantum dots and the resulting quantum confinement, and surface states on quantum dots. Porous silicon also displays electroluminescence, whereby the luminescence is induced by the application of a small voltage across electrodes mounted on the silicon, and cathodoluminescence from bombarding electrons.
Quantum effects

Quantum size effect
「量子尺寸效應」

Quantum confinement effect
「量子侷限效應」

mesoporous materials, etc
Nanowire Growth Mechanism

- Vapor-Liquid-Solid
- Melt injection into porous templates
- Electrodeposition into porous templates
Fabrication of Porous Anodic Alumina Templates

1. Aluminum
2. Anodize
3. Acid
4. Remove excess Al
5. Sputter Au
6. Remove barrier layer
7. Al₂O₃
8. CuCl₂
9. H₃PO₄
利用陽極處理氧化鋁 (Anodic Aluminum Oxide, AAO) 製造各式尺寸的奈米孔洞模板，孔洞的直徑分別為圖 (a) 60nm (b) 60nm nanopore template 的側面圖. (c) 20nm (d) 10nm.
Electrodeposition of Bi2Te3 nanowire arrays
Synthesis of Bi$_2$Te$_3$/alumina nanocomposites

Hexagonal Bi$_2$Te$_3$ single-crystal nanowires.


Bi$_2$Te$_3$ nanowire arrays (~45 nm)

( Xiaoguang Li, Hefei, P. R. China)

Hexagonal Bi$_2$Te$_3$ single-crystal Nanowires.

6.2 Nanostuctured Crystals

- Natural Nanocrystal
- B12

*Figure 6.22.* The icosahedral structure of a boron cluster containing 12 atoms. This basic unit of a number of boron lattices.
Fullerence C60

Figure 5.8. Structure of the $C_{60}$ fullerene molecule. The crystal lattice unit cell of $C_{60}$ molecules (large spheres) doped with alkali atoms.