Transactions of the Materials Research Society of Japan 33[2] 215-220 (2008)

Characterization of Functional Nano-Materials

YangKoo Cho[1], Hwackjoo Lee[1], Saechae Jeoung[1],Moonsup Bae[1]

Jeongsun Kim[2], Seungho Kim[3], Kweonha Park[4], Youngnam Kim[5]

[1]Division of Advanced Technology, Korea Research Institute of Standards and Science; #1 Doryong-dong, Yuseong-Gu, Daejon 305-340 Korea
[2] Materials Chracterization & Evaluation Lab., Agency for Defense Development, Yuseong P. O. Box 35-5, Daejeon, 305-600, Korea
[3]Korea Research Institute of Bioscience and Biotechnology, Yousong-gu, Daejon 305-806 Korea
[4]Korea Marine University. Youngdo-gu, Busan 606-791 Korea
[5]NPC Co. Ltd. Bong-dong, Wansan-gun, Jonrrabuk-do Korea

Contacting Author: Yangkoo Cho is with Division of Advanced Technology, Korea Research Institute of Standards and Science; #1 Doryong-dong, Yuseong-Gu, Daejon 305-340 Korea (phone:82-42-868-5850; fax: 82-42-868-5047; e-mail: ykcho@kriss.re.kr).

Abstract—Highly functional nano metal powders such as Ag,Au,Cu,CuNi and CuAg were developed using a specially designed RF plasma synthesis equipments operating at 20kW and 13.56MHz and their material properties were characterized. In the examination of their morphology by TEM and SEM, the nano metal powders had a perfect round shape with either ball type or hollow type, depending upon their cooling rates. In order to ascertain whether a single nano powder is ball type or hollow sphere, it was drilled out by fs-laser. Very large size hollow spheres were found. They showed the strongly affirmative behaviors to human body by the subsequent evaluation experiments. It was found that the nano metals were not oxidized under the atmospheric environment. These kinds of property changes were directly confirmed by their magnetic properties.

Key words: Nano material, RF plasma, hollow, CuNi, Silver powder

1. Introduction

A material's composition, the structure and its functions can be changed from their original bulk properties to other properties because of its small and/or intermediate size through size reduction process on an atomic scale. Many efforts have been paid to develop nano-sized metal powders by using the various kind of chemical and /or physical methods like sol-gel process, chemical vapor condensation method, thermo-chemical process and so on. However it is not satisfactory to get very homogeneous, clean and round shaped nano particles that can be applicable to bio use.

Recently we succeeded to develop highly functional nano metal powders efficiently by using a specially designed RF plasma method. The obtained nano metal powders show a quite different material property compared to its bulk one. Various kinds of nano sized metal powders (Ag, Au, Cu, CuNi, CuAg..)are developed based on RF plasma technology. The nano particles show a perfect round shape with ball type and hollow type by depending on the cooling rate. To ascertain the vacant Ag ball (hollow), we drilled a hole using special designed *fs*-laser opto-perforation to Ag nano particle. The obtained SEM photograph shows a clear evidence of vacant structure of inner shell.

The obtained EDS spectra show the clear evidence of clean metal surface without any oxide formation. The solidified inner core in Cu-Ni powder, which was the last portion to solidify would be extra-rich in copper. It is important to identify whether the nano composites have the homogeneous or the cored structure. Thus, we have examined them by a quantitative EDS and EELS chemical analysis techniques using nano probe in TEM.

The magnetic properties for CuNi nano metal powders are measured. The magnetization is remarkably higher than the bulk value and is enormously enhanced with decreasing the particle size. This giant magnetic moment in the nano particles is most likely to be associated with the Langevin-type super para-magnetism, which is supported by the weak hysteresis and the ferromagnetic-like behavior. The results can be understood within a framework of uncompensated spin and/or surface anisotropy. The magnetic data suggests that the CuNi nano particles produced by the plasma method results in significantly less oxidized metallic states than those by the other techniques. The CuNi nano particles prepared by the chemical method make a drastic increase of magnetization at low temperatures due to the oxide layer on the surface of nano particles.

Regarding the bio affirmative with human body, *In-vivo* test of nano gold and silver powder was conducted to Normal human dermal Fibroblast(NHDF), human Gingibal Fibroblast (HGF), Aquamous Carcinoma cell (SCC), Stoma Carcinoma cell, Hepato Carcinoma cell (HepG2) and Breast Carcinoma cell (MCF+). All the results show strong bio affinity of nano metal powders.

The potential application of nano metal in fluids are also investigated by measuring the thermal conductivities ratios. The obtained results show about 150% increase with nano fluid having 1.0 vol% of CuAg nano particle and almost 40% increase with 1.0 vol% of CuNi nano particle. It can be estimated that nano metal powder is one of the strong candidate of heat exchange material.

2. Sample preparations

Figure 1 shows schematic view of RF plasma reactor system for synthesizing nano metal powders. RF power was supplied with 13.56MHz up to 20kW. Powder feeding system(2) was specially designed to maintain stabilized powder transfer by Ar carrier gas during raw material feeding process. RF impedance was changed with the variance of solid powder transfer within the plasma environment. To avoid plasma fluctuation during feeding, we also designed real time RF matching system(4). This attachment makes possible to enhance powder quality. Before adopting this matching box, we paid much effort to separate desired size particle from whole products. After passing through plasma reaction torch, the melted raw materials are cooled down as the career gas flows downward. We installed several gate valves located at the position of 2m and 4.5m to get the size-oriented nano powders easily(10).

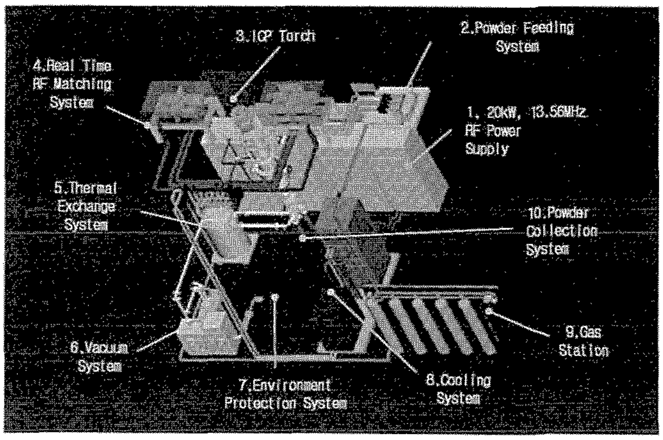

Fig 1. Schematic view of RF plasma reactor system. 1. 20kW, 13.56MHz RF Power Supply, 2.Powder Feeding System, 3. ICP Torch , 4.Real Time RF Matching System, 5.Thermal Exchange System, 6.Vacuum System, 7.Environment Protection System, 8.Cooling System, 9.Gas Station, 10.Powder Collection System

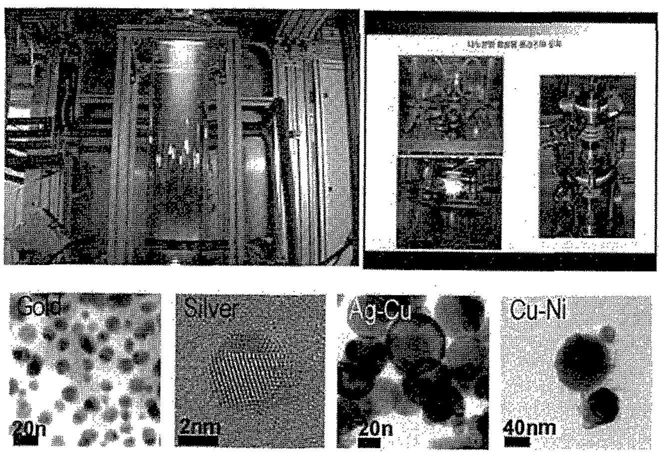

Fig 2 A photograph of RF plasma powder synthesizer. (Upper) TEM images of obtained metal powder, from left to right Au,Ag, Ag-Cu, Cu-Ni respectively(Bottom)

Figure 2 shows actually operating plasma view(upper left). Green colour represents plasma spectrum of Ag. The upper right photograph shows the various kinds of torches used in experiment. These torches are RF-RF double torches. If we want to increase reaction efficiency, it is necessary to hold time so as to stay raw material at high temperature region. RF thermal plasma method have following merits : 1) able to synthesize high purity nano powder due to the higher energy density, rapid quenching rate, bigger plasma diameter, and reacting material resides longer time period inside plasma 2) scaleable and efficient synthesis method from small to large quantity.

Other methods (DC-RF, Wire Feeding Explosion, Chemical Gas-phase Synthesis, Liquid Phase Synthesis, Mechanical Deformation Synthesis) have several problems, including the low density, irregular shape, instability, low yield rate, environmental pollution, oxidization, low purity, explosive, etc. Adoption of higher frequency (by using 13.56 MHz compared to 4 MHz of current technology, achieve higher energy and plasma density)

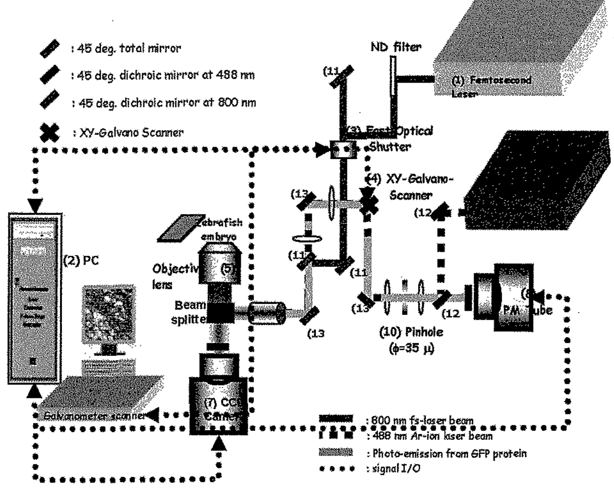

Fig 3 Schematic view of femto-second laser fabrication system

leads to higher yield rate of 60%~70% (compared to 10% yield of 4 MHz ones) and applicable to metals and ceramics. Furthermore it is very easy to control the shapes and sizes of obtained nano powders. If we want to get bio affirmative nano powders, it is absolutely necessary to increase clean reaction area. Quartz material was used to contain plasma atmosphere.

The obtained nano powder shows the high surface stability in the air or liquid at room temperature. Each particle does not react with each other. Especially, the obtained metal powders are extremely stable in the air even though generally metallic powder in nano size can be explosive easily.

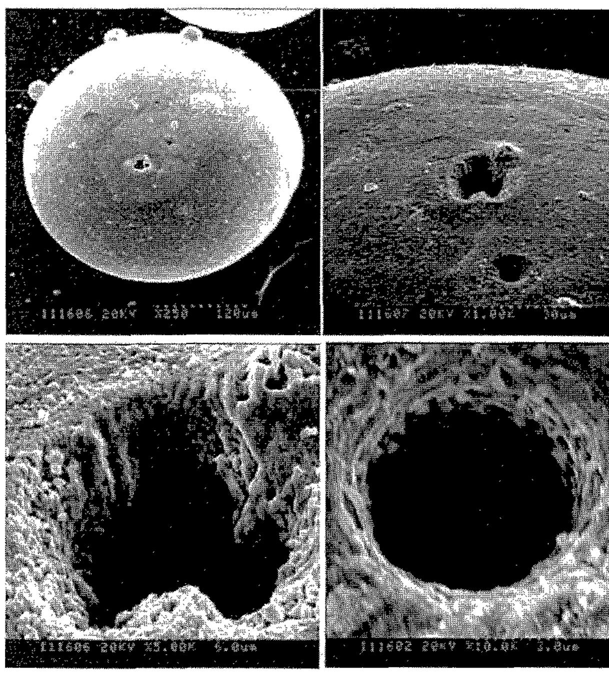

Fig. 4 Feasibility test on the formation of via-hole drilling by fs-laser processing. Actually, we found a direct evidence for the presence of the hollow in the supplied metal spheres with a wall thickness of 3-4 micro meter.

3. Morphology observation

Recently the appearance of reliable ultra-fast laser enables us to be used for laser-induced micro fabrication without any melting interfaces.[1-4] We decided to apply this method to metal nano powders to observe core structure. A linearly polarized femto-second pulse was used to ablate the metal surface. Figure 3 shows overall view of adopted femto-second laser system. To prevent the effect of successive sub-pulses, single shot configuration was adopted in this work with the use of a fast mechanical shutter. The ablation of metal powder surface was performed by a Ti:sapphire laser (Quantronics, USA) in air. This laser delivers pulses with energy up to 1mJ at 800nm and a repetition rate of 1kHz. The fundamental output of the laser was delivered to the galvanometer scanner (Scanlab AG, Germany).

Drilling process by pulsed laser was conducted 20~30 times continuously to prevent thermal diffusion of surface. Minimal thermal effects due to minimum absorption and thermal diffusion lengths reduce melting zone even at NIR laser pulse. This method is known as "optical chisel". Figure 4 shows obtained results on the formation of via-hole drilling by fs-laser processing. Actually, we found a direct evidence for the presence of the hollow in the obtained metal spheres with a wall thickness of 3-4 micro meter. So far, many researchers have been investigated the sol-gel method to synthesize the hollow spheres. However it is very difficult to get large size hollow sphere only by wet process. We can control their diameter from several nm to several hundred micro meter.

4. Surface Analysis

Nano-sized composites of Cu-Ni have been produced by an inductively coupled plasma reactor equipped with the LN_2 cooling system. Those of the starting raw materials were 50Cu:50Ni (at.%). The Cu-Ni alloy was assumed to have the cored structure by non-equilibrium freezing from the Cu-Ni phase diagram. The surface (hereafter, called as edge) of Cu-Ni powder, which was the last portion to solidify, inner area, would be extra-rich in copper. It is important to identify whether the nano composites have the homogeneous or the cored structure. Thus, we have examined them by quantitative EDS and EELS chemical analysis techniques using nano probe in TEM JEM-3000F (EDS, EELS, Holography). The observation condition is as follows;

-Collection angle:10mrad
-Diffraction mode
-Dwell time<500msec, (vs. EDS ~ 10 – 20sec)
- Beam probe size (1nm)
- Displacement steps (2-6nm); edge to center

In order to check the reliability for analyzing chemical composition, we analyzed the well-grown NiO nano single crystal of {100} plane facets (Figure 5a). Fig 5b shows its EELS spectrum. The results of EDS and EELS quantitative analysis showed nearly the same as 48.5at.% Ni, 51.5at.%O and 48.8at.% Ni, 51.2at.% O, respectively. Cu-Ni nano-crystalline particles were produced as spherical shapes and various sizes from 10nm to 200nm. The Cu-Ni alloys have been made as a fully solid solution in a wide range of the compositions in an isomorphous alloy system. For the quantitative EELS linear profile nano analysis, we focused on Cu-Ni nano composite powders. Fig. 6 shows their linear EELS profile spectrums of Ni L23–edge (~850eV)[5] and Cu L23–edge (~933eV)[5] across a CuNi powder of 16nm in radius from edge to center. The surface area of CuNi alloy is greatly rich in nickel and lack of cooper while the copper contents gradually increases around the center of the alloy. The mean free path of Cu and Ni were calculated as about 120nm at 300keV[6]. In general, if $t/\lambda>1$ (t: thickness, λ: mean free path),

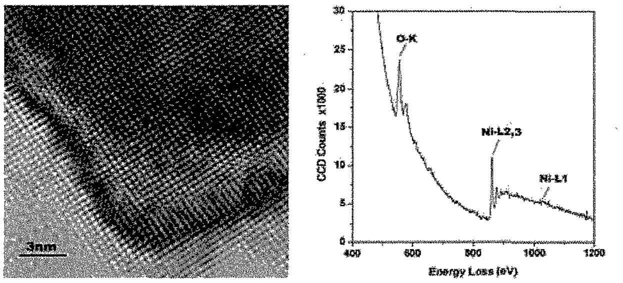

Fig. 5 HREM image of an NiO nano cuboidal particle of 30nm, well grown single crystal of {100} plane facets (a), and its EELS O-K and Ni-L2,3 edges for quantitative analysis, and no Cu-L2,3 edge shows in EELS (b).

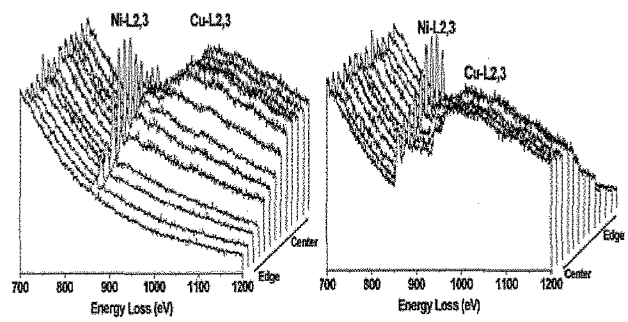

Fig 6 Quantitative EELS nano probe anlaysis for an linear concentration profile across a CuNi nanocomposite of 16nm in radius from edge to center (a). The spectrums shown in (b) represent the reverse order of (a) spectra.

the effect of multiple scattering should be considered, Fourier-ratio method has been applied to the thicker particles.

Figure 7 shows the obtained result from EDS. Point A is almost surface area of powder and point B is 2 nm apart from the surface. Both of points do not show any oxidation peak.

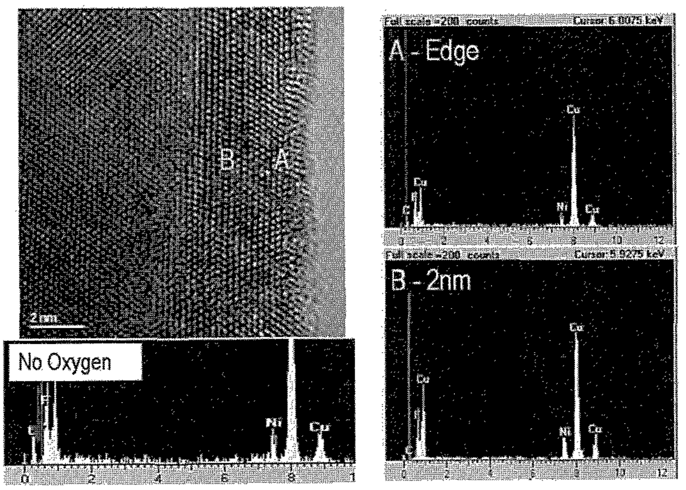

Fig. 7 Surface characterization of the synthesized CuNi nano powder using HR-TEM and EDS system analyzed points is not observed any oxygen peak

Therefore when we investigated microstructure and chemical composition in the surface layer of nano powders using EDS method, no oxide layer was found. EDS quantification results revealed very high spatial resolutions of 2 nm wide.

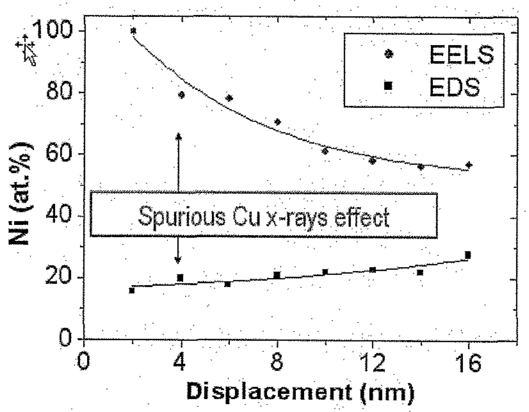

Fig. 8 Ni concentrations (at.%) across a CuNi nano spherical powder from edge to center. (EELS data were obtained from the Fig 6)

The EDS results were shown the results as the prediction on the Cu-enriched compositions on the edge. However, it should be careful in analyzing the EDS results because they collect the spurious x-rays originated from larger area of specimen, Cu grid, and the column of microscope as instrumental artifacts. However, the EELS spectrum has been collected from the almost nano probe area to eliminate the copper spurious x-rays[7].

Figure 8 shows the data comparison between EDS and EELS quantitative analysis. By using EELS nano analysis, we have obtained more sensitive and reliable data than those from EDS, especially, in the case of the cored inhomogeneous structure and of the chemical analysis for smaller powders less than 100nm. Furthermore, we have found that the Cu-Ni nano composites have had an opposite concentration profile between surface and center unlike the prediction on non-equilibrium solidified cored structures originated from Cu-Ni phase diagram.

Figure 9 shows the geometrical reason caused by spurious Cu x-ray effect. While the electron path of EELS method is quite simple, EDS receives many kinds of backscattered or fluorescent x-ray by geometrical electron beam path. This kinds of spurious x-ray causes degradation of spatial resolution as well as inducing artificial Cu x-ray. Therefore it is absolutely necessary to calibrate EDS system using standard sample before analyzing nano powder chemical composition.

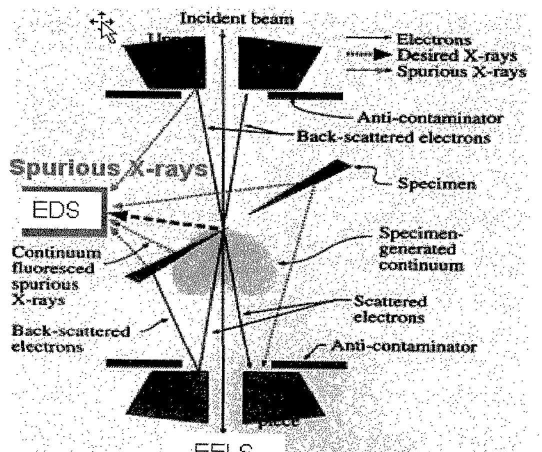

Fig. 9 Generation of spurious X-rays in EDS measurement

5. Magnetic property measurement

The magnetic property for various nano metals powders(Ag, Ag hollow, CuNi) are measured by using of Magnetic Property Measurement System MPMS-XL, Quantum Designas.

Firstly we tested raw material Ag(flake shape with few micron size), large size Ag(round shape with few hundred nm) , small size Ag(round shape with below 100nm) and hollow Ag(mean diameter is several hundred nanometer) as a function of temperature(T=20 K, 100 K, and 300 K) and magnetic field(H=10,000 Oe) respectively as shown in Fig. 10. All the measuring processes were conducted periodically under the same temperature to check material hysteresis.

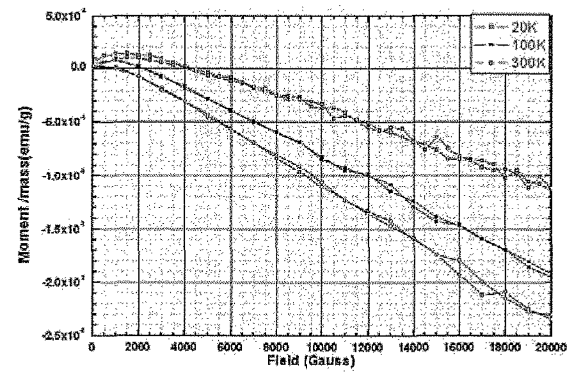

Fig 10 Magnetization measurement of Ag raw material as a function of magnetic field with three different temperatures.

For raw material Ag, mass magnetization M is increasing as a function of magnetic field with three different temperatures. It shows maximum value at 2,000Oe and its value gradually decreases up to 0 at 4,000Oe(dM/dH<0). If applied field is larger than 4,000Oe, It shows negative value(H>4,000Oe). There is no magnetic hysteresis.

Figure 11 shows magnetization value of plasma processed Ag nano powder as a function of magnetic field with three different temperatures. Magnetic property shows somewhat different manner. Magnetization values show rapid increase until magnetic saturation point. However its value show low-dependency of magnetic field over the saturation point. For the case of temperature at 20K, while plasma processed nano powder Ag shows positive magnetization value(M>0), on the contrary to this, raw material Ag shows negative value(M<0). The difference of magnetization value(dM/dH) between these two values is almost 3~4 times larger than that of raw material.

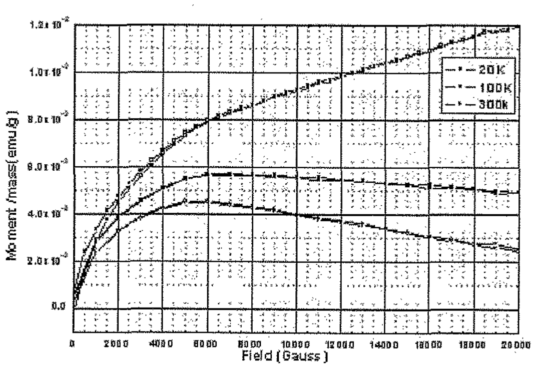

Fig. 11 Magnetization measurement of plasma processed Ag nano material

This change was caused by the drastic size reduction of nano powders. The same magnetic measurements were conducted to CuNi alloy system.

Figure 10 shows the same magnetic measurement results for various kind of Cu alloy with different processing method.

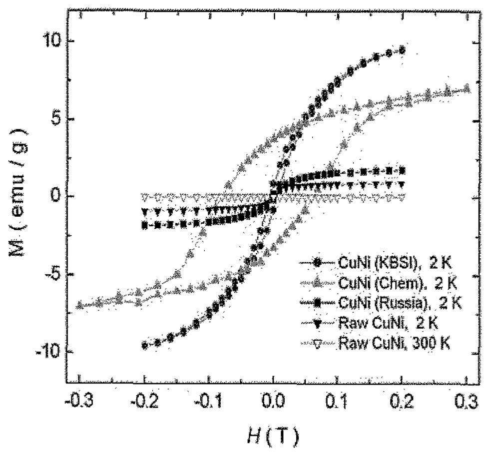

Fig. 12 Magnetic hysteresis measurement for various kinds of CuNi powders.
Notations of CuNi(KBSI), CuNi(Chem), CuNi(Russia) and Raw CuNi represents NPC Co. processed sample at KBSI(Korea Basic Science Institute), chemically synthesized powder using silver nitrate solution, imported Russian CuNi powder synthesized by Arc method and commercial CuNi powder synthesized by Arc method respectively

The magnetization is remarkably higher than the bulk value and is enormously enhanced with decreasing the particle size. This giant magnetic moment in the nano particles is most likely to be associated with the Langevin-type super para magnetism, which is supported by the weak hysteresis and the ferromagnetic-like behavior. The results could be understood within a framework of uncompensated spin and/or surface anisotropy. The magnetic data suggests that the CuNi nano particles produced by the plasma method results in significantly less oxidized metallic nano particles than other techniques, whereas the CuNi nano particles prepared by the chemical method makes an sudden increase of magnetization at low temperatures due to the oxide layer on the surface of nano particles.

6. Bio affirmative test

Silver has been proved to sterilize all single cell pathogenic bacteria in the world without any harmful side effect. As a result it prevents the plaque formation caused by bacteria fundamentally. By this reason many dental paste containing Ag powder are producing and sales everywhere. Recently many country aware of safety problem about Ag power. Especially ISO 229, OECD committee and EU nano strand project prepare the detailed regulations of various kinds of nano particle including Ag and Au as a hazardous material. Therefore to evaluate nano particle to human body and understand exact phenomena is very important.

Regarding the bio affirmative with human body, In-vivo test of nano gold and silver powder were conducted to Normal human dermal Fibroblast(NHDF), human Gingibal Fibroblast (HGF), Aquamous Carcinoma cell (SCC), Stoma Carcinoma cell, Hepato Carcinoma cell (HepG2) and Breast Carcinoma cell (MCF+).(Fig. 13). All the results show strong bio affinity of nano metal powders.

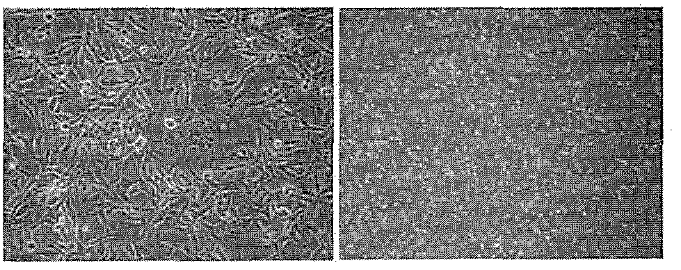

Fig. 13 *In-vivo* test of nano Ag powder for Breast Carcinima Cell(ER-) Reference sample(left) and after Ag nano powder contacted (Right)

In this test, we confirmed that Ag is still strong sterilizer again. However our human body are composed by numerous cells. It is necessary to approach more carefully.

7. Thermal conductivity measurement

Heat transfer effects of nano fluid processed by metal nano powder show very large increase of efficiency. To understand exact phenomena is very important to develop particular application fields. Potential mechanisms are assumed quasi-lattice growing on the nanometer particle surface which has unstable unpaired electrons or phonons, thereby enabling much faster heat transport in the layer than in the bulk fluid. And macroscopic lattice vibration or Brownian motion of the grown nano-particles, possibly direct solid-solid heat transport, which looks like phonon movement. Therefore enhancement of heat transport with free electrons was caused by nanometer powder. Finally the nano particles layering on and penetrating into a wall enhance the heat transfer on the surface and inside of a wall, respectively. The experimental data shows good evidence to these assumptions.

Table 1 Thermal conductivity and comparison of conductivity ratio as a reference of ethylene glycol value.

Materials	Thermal conductivity (W/mK)	Conductivity ratio
Diamond	900-2320	3600-9280
Ag	429	1716
Cu	401	1604
Ni	90.7	363
Ethylene glycol	0.25	1

When various nano powders were dispersed in ethylene glycol, its thermal conductivity were compared with that of corresponding bulk materials(Table 1). Diamond shows almost 3,000 times larger value of thermal conductivity than that of sample processed ethylene glycol.

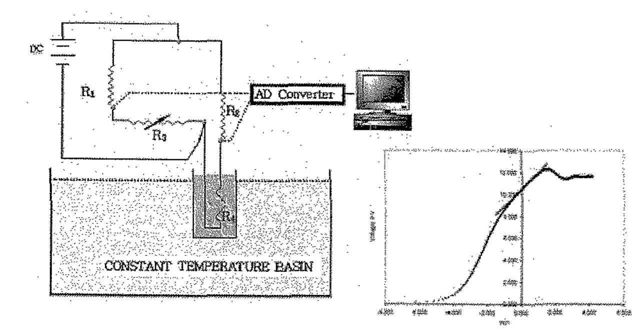

Fig. 14 Experimental setup for transient hot wire measurement

It is very difficult to measure the thermal conductivity of fluid due to the evolution of convection current. Therefore it is absolutely necessary to measure very quickly within 3 or 4 seconds so as to avoid convection current. Fig. 14 indicates the experimental setup for transient hot wire measurement.

	CuNi	CuAg	Diamond
Averaged nanoparticle diameter(nm)	30	30	10
Volume percent(%)	0.2 0.3 0.4 0.5	0.055 0.080 0.100	0.01
Temperature range(°C)	10 20 50	10 20 50	20

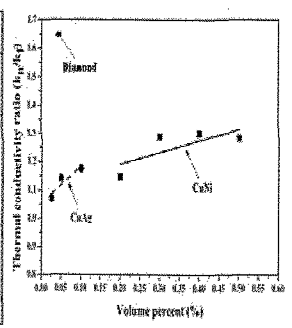

Fig 15 Thermal conductivity ratio at various temperatures from 5°C to 50°C

All the experiments were conducted under the conditions of normal state. The obtained data were averaged after 5 time measurements. Figure 15 shows thermal conductivity ration of Cu alloys and diamond at various temperature from 5°C to 50°C.

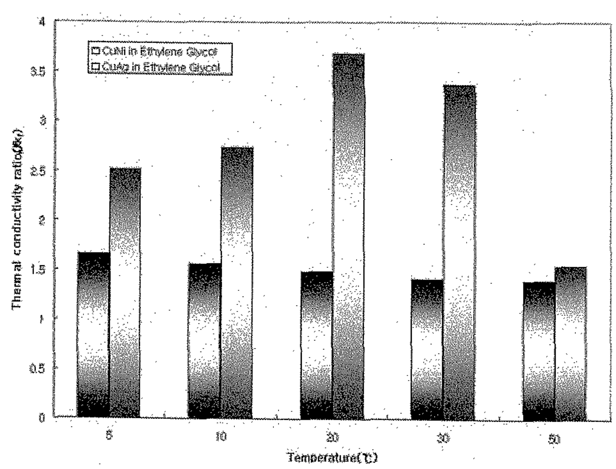

Fig. 16 Thermal conductivity ratio measured for nanofluid having 1.0 vol% of nano-powder

The obtained results show about 150% increase with nano fluid having 1.0 vol% of CuAg nano particle and almost 40% increase with 1.0 vol% of CuNi nano particle(Fig. 16). It can be estimated that the nano metal powder is one of the strong candidate of heat exchange material.

8. Summary

Summarizing the above experimental observations, the unique features and the advantages of nano powders are as follows.

1) Nano metal powders are produced based on the nano and plasma technology.
2) They have a spherical or a spherical hollow shapes and they showed the better material properties than the conventional nano powders with spike and flake shapes.
3) The nano powders are highly stable both in the air and liquid at room temperature.
4) Automatic control for the size distribution of 10~100nm was obtained in order to specialize and sustain nano powder's property.
5) Non-oxide nano powder was obtained. In general, metal powder immediately forms oxide layer by combining the oxygen in air. However, the obtained nano powder does not form oxygen layer in the air and also when exposed to moisture.
6) They showed the ultra para-magnetism against normal metal, no agglomerate and aggregate at room temperature
7) The obtained nano powder are affirmative with human body and dispersible in water or hydro-carbon liquid without particle surface treatment; cladding, oxidation, additive and any surfactant.
8) It can be estimated that nano metal powder is one of the strong candidate of heat exchange material. The potential application of nano metal in fluids are also investigated by measuring the thermal conductivity ratios.

ACKNOWLEDGMENTS

This research work was carried out in part with the support of the Ministry of Science and Technology of Korea under the project of Development of Advanced Scientific Analysis Instruments.

REFERENCES

[1] P.P Pronko, S.K. Dutta, S.Squier, J.V. Rudd, D,Du and G Mourou Opt. Comm. 114, 106 (1995)
[2] J.P.Sylvestre, A.V.Kabashin, E.Sacher, M. Meunier and J.H.T.Loung J. Am. Chem. Soc. 126, 7176 (2004)
[3] F.Mafune, J.-Y Kohno, Y. Takeda and T. Kondow J. Phys. Chem. B.106, 7575 (2002)
[4] J.P.Sylvestre, S.Poulin,A.V.Kabashin,E.Sacher,M.Menier and J.H.T.Loung J.Phys.Chem.B 108, 16864 (2004)
[5] C. C. Ahn,. and O. L. Krivanek, *EELS Atlas*, 28-29.(1983)
[6] T. Malis, S. C. Cheng, and R. F. Egerton *J. Electron Microsc. Technique* **8**, 193 (1988)
[7] D. B. Williams and C. B. Carter "Transmission Electron Microscopy," *Plenum Press*, New York and London, 682. (1996).

(Recieved January 16, 2008 ; Accepted March 2, 2008)