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APPLICATION OF INERT GAS CONDENSATION

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ABSTRACT

Over the last few decades, the production of nano-size powders has been achieved using various techniques. While there are techniques such as flame pyrolysis and chemical vapor deposition, inert gas condensation is one of the simplest processes and is still being used to produce nanopowders. The inert gas condensation technique has been known to produce various ceramic and metal nanopowders such as iron oxides, gold, manganese. The process is also able to produced magnetic fluids comprised of iron and cobalt-based nanoparticles.

1. INTRODUCTION

To understand how particles are produced by the inert gas condensation, the basic structure of the reactor and process will be explained and is based on the lecture notes provided by Professor Bernard Kear of Rutgers University. An inert gas condensation reactor has three main components: a crucible, vacuum chamber, and a cold substrate.[1] The crucible is resistively heated to evaporate the particles within the reactor. The vacuum chamber is filled with an inert gas, usually helium or argon, and is back-filled at low pressures, typically between 1 – 20 torr. The purpose of the cold substrate is to collect nanoparticles once they are formed in the system.

The crucible is heated to evaporate the raw materials. The nanoparticles, typically metal based, begin to form in the region above the crucible due to homogeneous nucleation. The interaction of the evaporated particles and the inert gas of the chamber is what causes the

nucleation to occur. The particles travel from the supersaturated region of the crucible to the rotating cold substrate by convective flow inside the reactor. The particles cling onto the cold substrate and growth of the particles concludes. These particles are then scraped of the cold substrate and collected. *Figure 1* shows a basic outline of the inert gas condensation reactor.

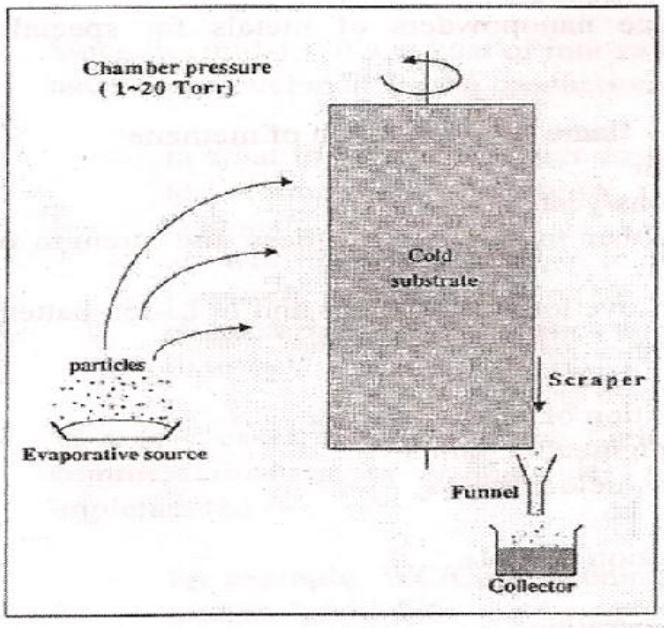

Figure 1: Inert Gas Condensation Chamber.

The size of the nanoparticles formed can be controlled by altering various parameters of the process. The inert gas used in the process is a key factor to the size of the particles. *Figure 2* compares particle diameter of aluminum and copper particles based on various inert gases and chamber pressures. Helium, argon, and xenon gases were tested with a pressure ranging from 1 – 100 torr.

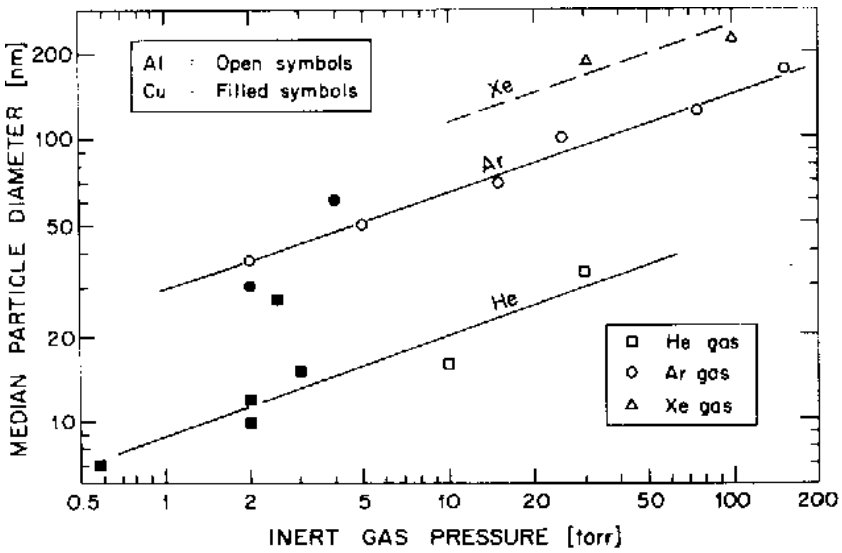

Figure 2: Al and Cu particle sizes made in various inert gases.

Particles made in a chamber consisting of helium gas had the lowest diameter. Copper particles produced in helium had an average size of 15 nm and were about 50 nm when produced in an argon environment. Aluminum particles produced in a helium filled chamber had an average size of 20 nm while the particles made in argon reached over 100 nm. Particles made in a xenon filled chamber reached diameters of 200 nm. The figure also shows how increasing chamber pressures will increase the diameter of the particles formed. The effect of the increasing pressure can be related linearly to particle diameter.

Various modifications have been made to the inert gas condensation process to increase the production rate of particles and narrow the distribution of particle size. The first modification introduced is a cross-flow of an inert cooling gas. This causes the particle clusters to quickly leave the hot region above the raw materials. The particles are then unable to aggregate.

A materials science research group from Technical University Darmstadt has used the inert gas condensation process over a variety of other powder processing techniques to form nanoparticles. In 1997, a group headed by N. Guillou was working on developing ceria nanoparticles using inert gas condensation. Guillou and group researchers aimed to show that former processing techniques such as sol-gel processing, electrochemical synthesis, and precipitating ceria from cerium nitrate solution would not yield the same high purity nano-sized particles as inert gas condensation. They also explore particles through out the entire vacuum chamber, not just the particles that settled onto the cold substrate. The group planned to determine if there is any difference in particle size between cold substrate particles and the rest.

2. Synthesis

Guillou's group began their synthesis process by taking cerium oxide powder and evaporating from a tungsten crucible in a helium gas environment.[2] The pressure of the chamber was kept constant at 1000 Pa. The cold substrate was set at liquid nitrogen temperature and the nanoparticles that settled onto it were oxidized by pure oxygen gas. Guillou broke down the particles collected into three groups: particles on the substrate, particles on the walls near the substrate, and particles in the surrounding of the evaporating boat.

They discovered that not all particles settle onto the cold substrate. Up to 50% of the ceria particles produced during the inert gas condensation process ended up on the walls or in the surrounding area. The particles found in different areas of the chamber were then taken and analyzed to determine grain size and distribution. Guillou discovered that particles found through out the vacuum chamber have a similar size distribution as particles found on the cold substrate.

Figure 3 shows the size distribution of the ceria particles produced by Guillou. It can be seen by on the graphs that the particles are all in the 3 nm range and particles on the cold substrate did not differ from particles on the walls of the chamber or in the surrounding region. The particles produced had a fairly narrow distribution as well. Most particles ranged from 2 – 5 nm in size. Guillou and the researchers expected no difference in properties between the particles taken from various areas of the chamber.

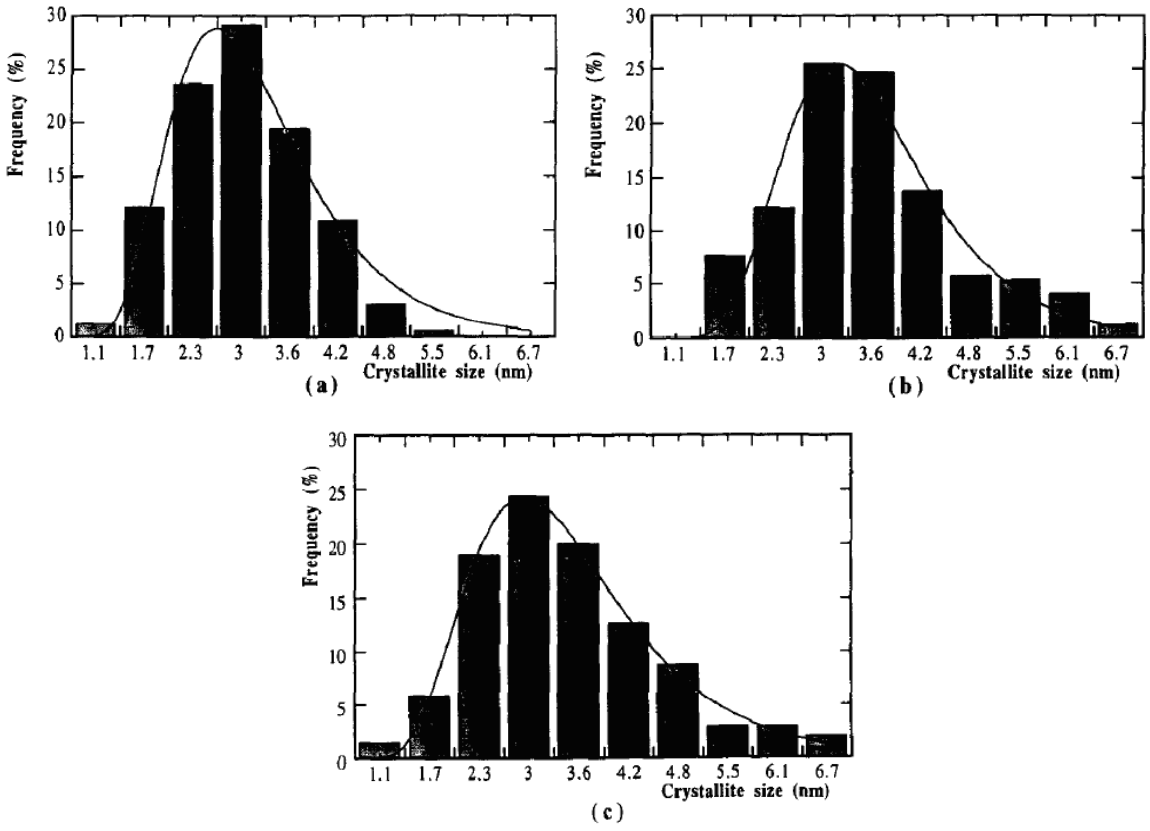

Figure 3: Particle size distribution of ceria particles, a) particles on the substrate, b) particles on the walls near the substrate, c) particles in the surrounding of the evaporating boat.

A group of researchers worked with silver and copper to produce nanoparticles using inert gas condensation. Their goal was to produce Ag-Cu nanoparticles and vary the evaporation temperature to determine if the temperature would affect particle size.[3] They began the process by taking silver and copper wire and twisting the two together rather then using a traditional powder source. The volume ratio of the two metals was 1:1. Like Guillou, Ceylan used a tungsten crucible to place his initial material. The wires were not placed directly onto the crucible but fed mechanically toward it. As the wire began to melt, the molten metal dropped onto the tungsten crucible and evaporates. As Professor Kear described, Ceylan used helium as the gas inside the chamber as it has the highest thermal conductivity of the inert gases. The research team was able to produce about 1 g/hr of Ag-Cu nanoparticles.

Figure 4 shows the particle size distribution of the Ag-Cu particles produced. Ceylan and his colleagues discovered that the evaporating temperature did not affect the size distribution of the Ag-Cu particles.

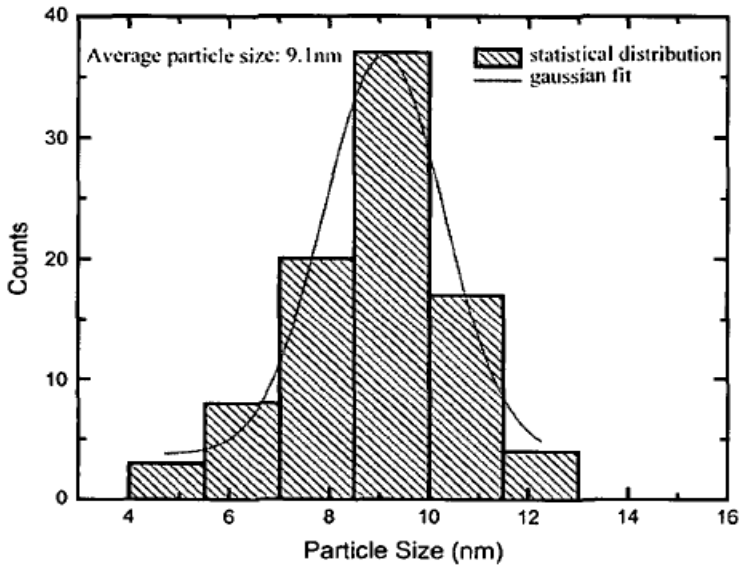

Figure 4: Ag-Cu particle distribution.

The particles had an average size of about 9 nm. Variation in temperature had an effect on Guillou's ceria nanoparticles though. As *Figure 5* shows the ceria nanoparticles produced became larger as the temperature was increased in the vacuum chamber.

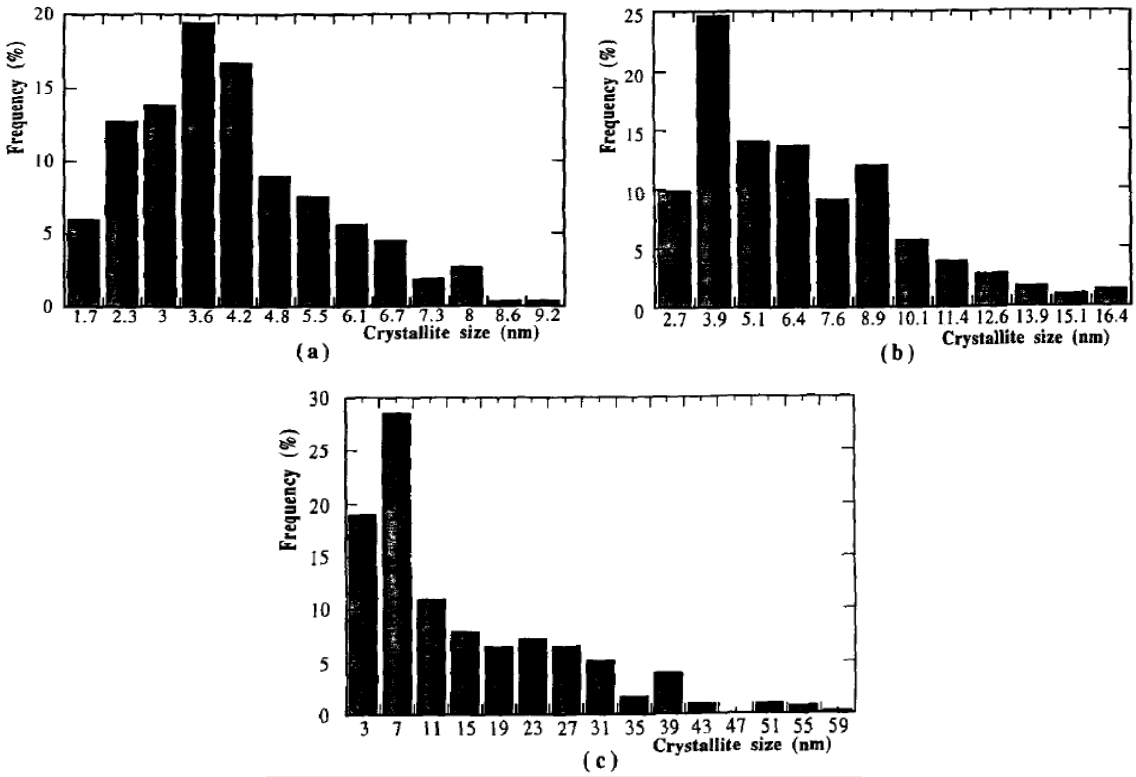

Figure 5: Ceria particle distribution as a) 400°C b) 600°C c) 800°C.

Ceylan's Ag-Cu particles are a silver matrix with a small percentage of copper within. The nanoparticles mostly produced were just silver and copper nanoparticles independent of the other. As shown in *Figure 6*, although the size distribution of Ag-Cu was not effected by the evaporation temperature, the volume percent of copper found in the Ag-Cu particles varied. At 1210 °C, the highest volume percent was recorded for copper in silver, 6.6%. As Ceylan explains, it is important to have the volume of copper as close to 7.5%, which is the amount found in sterling silver, as possible. Silver is corrosion resistant but soft, by the addition of copper the strength of the silver increases greatly.

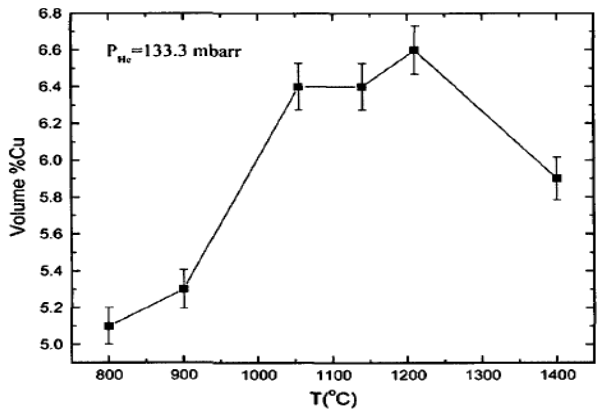

Figure 6: Copper volume percent in silver vs. evaporation temperature.

The particles made by Guillou and Ceylan both had an average size of under 10 nm. The inert gas condensation process has been able to produce nanoparticles of these sizes with very narrow distribution. M B Ward and a research group from the Institute of Materials Research at the University of Leeds have also been able to produce nanoparticles of manganese using inert gas condensation. The size of the particles they produced was of similar size of the Ag-Cu particles of Ceylan and ceria particles of Guillou.

Ward used a granule of manganese of 99.99% purity in a helium gas filled chamber.[4] A tungsten crucible was used to house the initial manganese granule. The chamber was backfilled with helium gas that passed through a liquid nitrogen cold trap to increase the purity of the helium. The pressure in the chamber is held constant at 40 mbar. This removes oxygen that can cause manganese oxide from forming during the process. The tungsten crucible was heated to 1260°C and the manganese evaporates out. Rather then using a normal rotating cold substrate, Ward used TEM grids to capture the nanoparticles and the system was cooled. The TEM grids were then removed from the chamber to be examined. *Figure 7* shows a schematic of the inert gas condensation system.

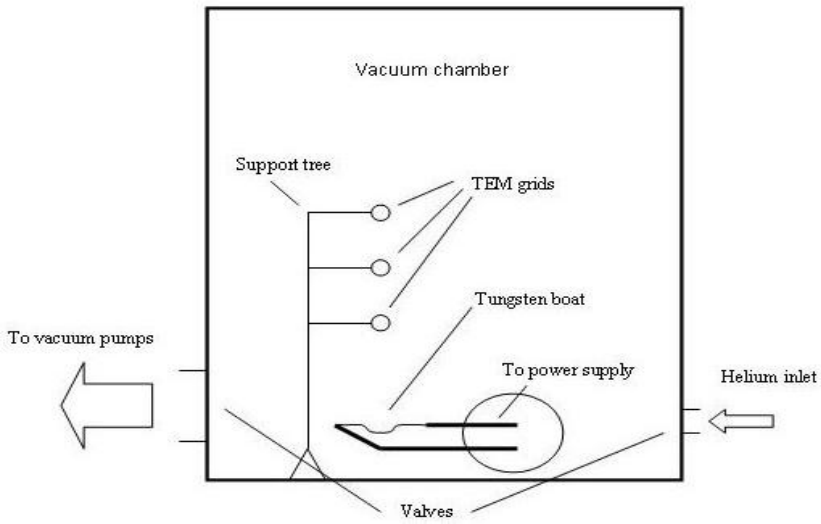

Figure 7: Inert gas condensation system.

When helium was not passed through the liquid nitrogen cold trap Mn_3O_4 was formed in the chamber. Ward goes on to say that this form of manganese oxide is not the most stable form at room temperature and that the temperature and pressure of the chamber produced this form. After passing the helium through the cold trap, a large portion of moisture was removed creating an atom ratio of Mn:O of 3.3:1. This was a great improvement of the original atom ratio of 0.7:1.

Like Guillou and Ceylan, a large amount of the particles are under 10 nm in size. *Figure 8* shows the particle size distribution of the manganese particles produced by Ward and his researcher group. The manganese nanoparticles averaged to be around 6 nm. It can also be seen in *Figure 8* that there is a fairly large amount of nanoparticles formed with size around 16 nm. Ward explains that these larger particles are connected in string.

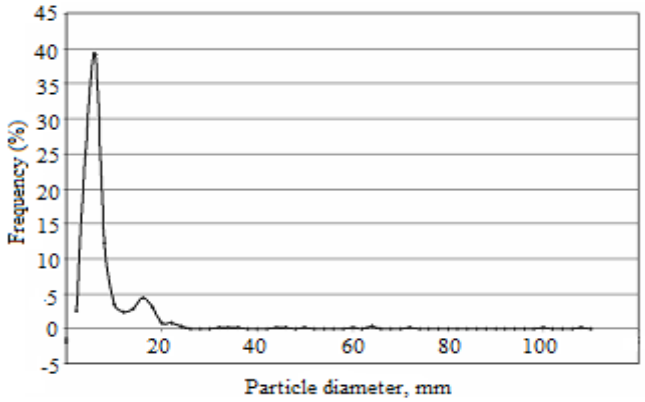

Figure 8: Particle size distribution of Mn nanoparticles.

Figure 9 shows a TEM image of the manganese particles formed by inert gas condensation. The small manganese particles are pointed out on the TEM image (a). Their size range from to 2 to 10 nm. The larger donut shaped clusters are the particles that range from 12 to 20 nm. These clusters have an outer layer which is denser then the inner portion. Some of the clusters have an empty center. The outer layer is approximately as thick as the isolated particles that are about 6 nm in size. This means the particles connected in a line fashion and then closed around on themselves.

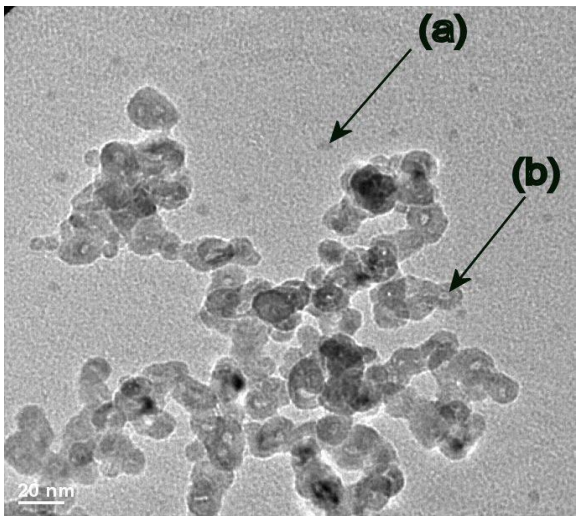

Figure 9: TEM image of Mn nanoparticles.

While the previous experiments attempted to hold parameters constant to find an average particle size, the next group decided to vary parameters to observe crystallization of the particles produced. A South Korean research team has been using inert gas condensation to produce tin (II) oxide nanoparticles using a mix of oxygen and helium gas rather then strictly helium.[5] An ultra pure tin shot (99.99%) that is 3 mm in size is heated in the chamber in a graphite crucible rather then the usual tungsten. The research group varied the pressure of the chamber to see the effect of on the crystallization. X-ray diffraction was used to analyze the samples produced.

Another research group from Spain has also been working on tin oxide nanoparticles. The experiments performed used a tantalum boat and used helium gas in the chamber. Jiménez and Spanish based group also varied the initial material to see the effects on the particle size. Pure Sn, SnO, and SnO_2 were all tested as part of the experiment with temperatures of 1100°C, 1000°C, and 1100°C respectively.[6] The pressure of the helium gas (99.999% purity) was held constant at 1 torr (~133 Pa). The particles evaporate and deposit onto a liquid nitrogen substrate.

Figure 10 is a pair of TEM images that show the tin oxide particles produced by Lee and the South Korean group. The first image was made in a chamber using oxygen gas exclusively of pressure 1.3 kPa. The second image is tin oxide nanoparticles made under an environment of gas that is a mix of helium and oxygen. The tin oxide particles fabricated were about 10 nm in size for both oxidation paths used. The nanoparticles made in exclusively oxygen gas appear to be a little larger than the particle made with the mixed gas.

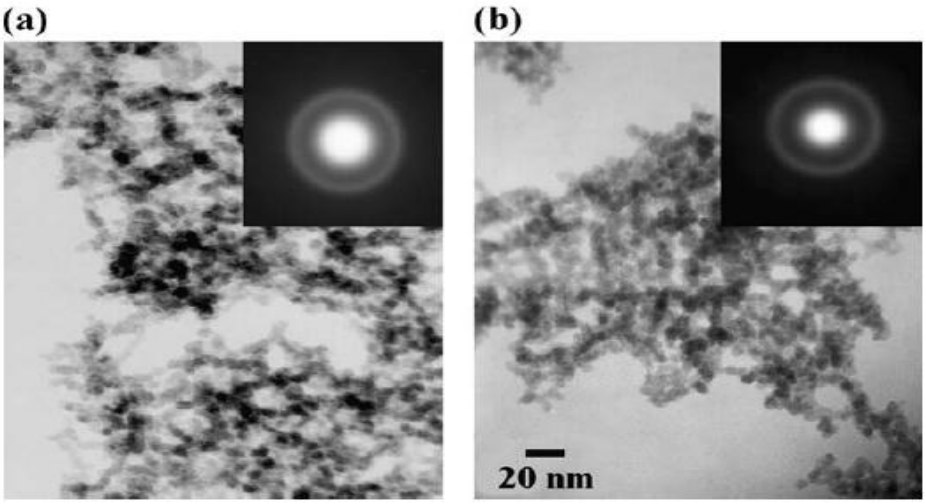

Figure 10: Tin oxide nanoparticles – a) 1.3 kPa oxygen b) 1.3 kPa oxygen and helium.

Jiménez and the research group from Seville, Spain were also able to fabricate tin oxide nanoparticles but had some problems originally. They first attempted the inert gas condensation at lower temperatures. As they did x-ray analysis, the diffraction peaks were very narrow. Jiménez describes this as particles that do not show nanomaterial characteristics. In *Figure 11*, although difficult to see, are tin oxide particles. In the bottom right corner of the image, individual tin oxide particles can be seen slightly. These were achieved by heating the chamber to 1100°C, same as researchers in South Korea used to produce their tin oxide particles. Jiménez goes on to say that the particles are only 10 – 40 nm in size rather then 10 nm or less made by Lee. They were able to use a lower pressure and similar temperature to make particles of size 8 – 10 nm. Both research teams were able to fabricate tin oxide particles of the same size.

Figure 11: Tin oxide nanoparticles.

Although some use argon or another gas in inert gas condensation, helium is traditionally used because of its great thermal conductivity. While working on Ag-Cu nanoparticles, Ceylan and his group also studied the thermal conductivity of the particles they produced. The nanoparticles of Ag-Cu were added to a liquid to enhance the thermal conductivity. Ceylan explains the mechanisms for thermal conductivity enhancement:

"These mechanisms include Brownian motion of the particles, molecular level layering of the liquid at the nanoparticle-liquid interface, ballistic heat transport in nanoparticles, and cluster formation of the nanoparticles."

They determined that the main source of thermal conductivity enhancement was cluster formation. *Figure 12* shows thermal conductivity against the amount of nanoparticles added into a fluid. As is shown, 006% volume nanoparticles of Ag-Cu in a solution increase the thermal conductivity the most. The fluid's thermal conductivity is 33% higher than it would be with pure oil. The thermal conductivity then sharply drops off down to the same value of oil. Ceylan also measured the viscosity of the fluid to determine how the nanoparticles will affect it. The research team came to the conclusion that the viscosity was not affected much.

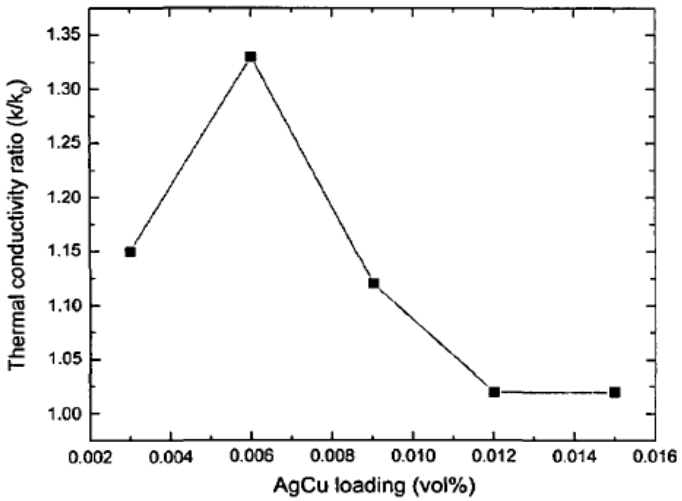

Figure 12: Thermal conductivity vs. Ag-Cu nanoparticles volume in a fluid.

All the particles that were discussed earlier that have been fabricated using inert gas condensation are stable particles. Two researchers from the Institute of Physics at the University of Saarbrücken worked on various metastable particles using inert gas condensation. Krauss and Birringer worked with tungsten, tantalum, and yttrium oxide powders. They set to show how inert gas condensation can be used to make these metastable powders that can hardly be synthesized by classical metallurgical processes.

The researchers evaporated pure yttrium particles in the chamber onto the cold substrate. The inert gas used is then removed from the chamber and oxygen is pumped in until it reaches atmospheric pressure. The particles produced were not completely oxidized from the inert gas condensation process alone, so the particles were removed and placed in a pure oxygen atmosphere at a temperature 350°C for approximately a half hour. This allowed the nanoparticles of yttrium oxide produced to completely oxidized and nano scale. Using x-ray diffraction they found these particles that were under 10 nm in size were not in an equilibrium state.

The tungsten and tantalum particles were made in a slightly different manner. They were not thermally evaporated like most powders. Instead, dc-sputtering was implicated to force the metal particles into their vapor phase. By using this process Kauess and Birringer were able to make tungsten and tantalum particles with average sizes of 12 nm. These particles were analyzed using x-ray diffraction and found to be in a metastable phase. All the particles produced were, normally unstable at room temperature, able to be stable.

3. CONCLUSION

Inert gas condensation can be used to create nanoparticles on many different materials. This process is the basis of the chemical vapor deposition process. Although the CVD process is now used for the fabrication, inert gas condensation is still used when making nanoparticles. By varying different parameters it is possible to make various particles under 10 nm in size with a narrow distribution. These particles can then be used in many different applications. Researchers will continue using processes like inert gas condensation to discover more materials which be brought down to the nanoscale.

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