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## Combined equipment for synthesis of ultrafine metals and metal compounds powders via Flow-Levitation and crucible methods.

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# Combined equipment for synthesis of ultrafine metals and metal compounds powders via Flow-Levitation and crucible methods.

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**Abstract.** Laboratory automated equipment for synthesis of ultrafine particles of metals, alloys and metal compounds via evaporation-condensation Flow-Levitation Guen-Miller method combined with crucible method using high-frequency (440 kHz) electromagnetic field for heating is described. The equipment synthesizes the said particles and multilayer core-shell structures with mean size ranging from tens to hundreds of nanometers with output from grams to tens of grams per hour. Synthesized particles may be collected into container with inert gas, or into non-volatile liquid, or *in situ* passivated with air for further handling. Examples of synthesized particles are presented.

## 1. Introduction.

Ultrafine (sub-micron and nano-sized) particles (UFP) of metals and metal compounds are of significant interest and in high demand for scientific research. They have an ample spectrum of applications ranging from production of high-energy nanocomposites to a wide variety of materials used in agriculture and biomedicine. The synthesis of metal and metal compound UFPs at nanoscale magnitudes ( $<D>=5-1000$  nm) is a proven complex exertion that requires meticulous consideration to countless parameters and mode adjustments to obtain the product at optimum conditions. These conditions often include chemical, phase, and granulometric characteristics and other requirements such as custom composition gradient, and non-agglomerative properties of the UFPs in order to achieve a more uniform distribution of the particles in a medium. Therefore, equipment to synthesize nanoparticulate must possess the necessary versatility and adaptability to accommodate the vast and often uncounted number of manufacturing requirements. The equipment should, for instance, be capable to manufacture nanoparticles using a wide assortment of metals, synthesize UFPs with a wide range of properties, facilitate a wide throughput spectrum, adapt to synthesis-technique modalities, uncomplicated and inexpensive maintenance, etc.

## 2. MIGEN Equipment description.

MIGEN equipment is based on the Flow-Levitation (FL) evaporation-condensation method invented by Guen and Miller [1-3].

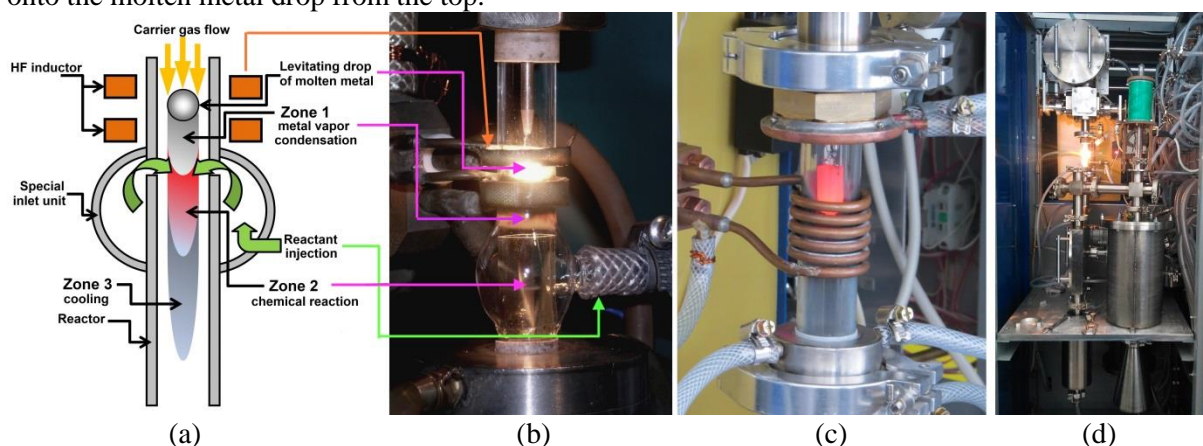
Figure 1 demonstrates the principle of the FL-method. A drop of molten metal levitates inside a quartz tube reactor where it is heated by the electromagnetic field of a high-frequency (~440 kHz) countercurrent inductor. The drop temperature is high enough as to provide an acceptable evaporation



rate of the metal. Evaporated material is continuously replenished using feed-wire at preset rates ranging from 1 to 100 g/h, depending on the metal and particle size required.

To synthesize alloys of desired composition, the apparatus is equipped with two independent mechanisms for simultaneous wire (0.4–1.0 mm in diameter) feeding. Wire feeding rates are set for each mechanism separately to provide mass feeding in the range 0.1...100 g/h with an accuracy of 0.1%. Coils of wires are placed inside a vacuum chamber of the apparatus. Wire is fed to the evaporating drop with stepper motor mechanism, placed outside of the said vacuum chamber to avoid undesirable contamination of the synthesized powder with the substances released by operating motors. Wire feeding mechanisms rotating shafts with driving rollers are passed from the motors into the vacuum chamber through vacuum-proof oil-free Wilson-type seals.

Inert gas or inert-reactive gas mixture of preset composition is continuously blown downstream onto the molten metal drop from the top.



**Figure 1.** Flow-Levitation method for synthesis of ultrafine particles: (a) – scheme of nanoparticles synthesis process, (b) – appearance of a FL-mode reactor with side reactant input; (c) – appearance of a crucible mode reactor, (d) view of actual equipment in operation

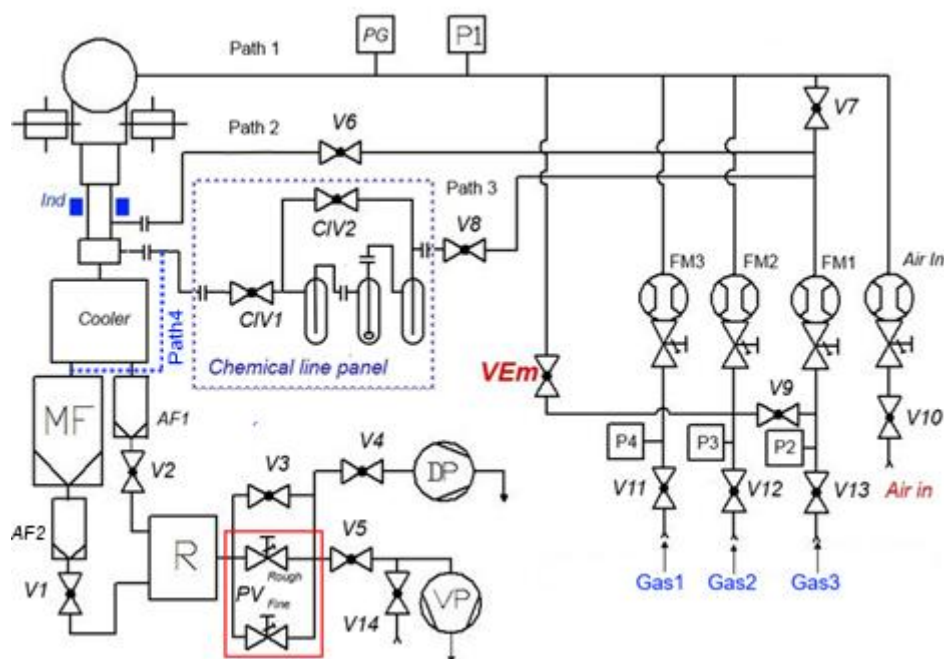
This method is known in general in other research groups. It is used in equipment assembled independently in Russia [4,5], Korea [6,7], Iran [8,9], India [10] and China [11–13].

Metal vapor condenses homogeneously within the gas flow below the drop, then fresh-formed nanoparticles are cooled and collected by a fabric filter or a bubbler filled with non-volatile liquid. The concentration of metal vapor in the gas, and its cooling rate determines the final size of the nanoparticles in this section. These parameters can be controlled by presetting the drop temperature (dependent on the wire feed rate), the type of inert gas (argon, helium, hydrogen etc.) and the pressure and velocity of the gas flow over the molten drop. Whereas diffusion coefficients, viscosities, thermal conduction and capacity of the said inert gases are strongly different from each other, the composition of the carrier gas influences not only on particle size and size distribution, but also on the morphology and crystallinity of the formed particles.

Desired physicochemical characteristics of nanoparticles and/or their surface are achieved by treatment of nascent particles with gaseous reactants injected into the gas flow carrying the condensing nanoparticles. Depending on chemical treatment regime (reactant concentration, temperature in the point of reactant injection), one can synthesize a metal compound, core-shell-structured particles (e.g. with metal core and metal compound shell), or metal nanoparticles with thin surface coatings of desired compositions.

Since a temperature gradient below the drop amounts to tens or hundreds of degrees per centimeter, it is possible to set the required temperature in the reaction zone from practically the melting point to the ambient temperature, by placing the intake of reactant gas at the proper distance  $L$  from the drop.

The reactant is blown in a chosen zone of the reactor through the pathways 1, 2, 3 or 4 (figure 2) at a distance  $L$  from the drop with the proper concentration to create the required conditions for chemical reaction with metal vapor or nascent nanoparticles.



**Figure 2.** MIGEN equipment gas scheme. V1-V14, CLV1, CLV2, VEm – vacuum ball valves, FM1...FM4 – flowmeters with gas flow control multivalves. MF – main fabric filter, AF2 – additional filter for use in transition regime, AF1 – emergency filter, P1...P4 – vacuum-meters, PG – membrane gas pressure gauge, R – receiver, PV – multivalve flow rate and pressure control valves, VP – forevacuum pump, DP – diaphragm pump

During synthesis of metal compounds, it is possible to admix simultaneously up to 3 reactants into the flowing gas. The reactant can be supplied at different points of the flowing gas: into the main gas flow, blowing around the molten metal drop (Path1, applicable only to synthesize metal compounds unstable at the drop temperature), downstream the gas flow at distances from 0.5 to ~20 cm from the evaporating metal (Path 2 and 3), into the outlet of the cooler (Path4). These reactant injection points provide the reaction temperature from that of the molten drop to practically room temperature. This allows variation of particles composition and synthesis of uniform compound particles as well as multilayer core-shell structures.

Both gaseous reactants and mixtures of liquid reactant vapors with inert gas may be used. In the last case, a desired evaporation rate of the reactant may be achieved by placement of the reactant containing bubbler into container with controlled temperature.

In instances where the brittleness, low melting point and poor electric conductivity of a material limits the usefulness of the FL method, MIGEN can be easily switched to crucible-based high-volume evaporation with HF heating, and no metal feed-wire. Brittle metals of interest, such as magnesium and manganese, are not available in the form of wire. This hampers the use of the Flow-Levitation method which relies on replenishment of material via feed-wire. Similarly, metals with melting point less than 400 °C get overheated in the electromagnetic field at the intensity needed to levitate the molten drop. The FL method in these cases renders extremely fast evaporation of the metal. Materials with poor electric conductivity also inhibit the use of the FL method since they cannot be levitated within the electromagnetic field.

Nevertheless, the cunning adaptability of the new generation of MIGEN equipment to crucible modality easily resolves the inherent, but minor, glitches of the FL method. The equipment is commercially available for production of a wide variety of nanoparticles (Figure 1). The technique modalities used by MIGEN (FL method and Crucible-based) are attained via exchangeable reactor assemblies (Figures 1c and 1d) that use common gas, reactant and power control of the manufacturing equipment. In both modes, the electromagnetic field generated by a tunable high-frequency (440 kHz) generator is used for heating and evaporating the metal.

The Flow-levitation mode is used for a majority of regular metals with melting point  $T_{\text{melt}}$  between 400 °C and 2000 °C and high electric conductivity. Quartz tube reactors, in which heating and evaporation of the metal take place, are available in diameters of 18 mm and 21 mm. The crucible mode is used for metals unavailable in the form of wire such as (Mg, Mn) and materials with poor electric conductivity (e.g., rare earth metals). The heating of the material sample is accomplished in quartz tube reactors with diameters 18, 21 or 30 mm using a unidirectional inductor. Crucibles for the material evaporation are made of carbon, glassy carbon composite (such as Sigradur), or refractory metals, such as W, and Ta. In addition, crucible method is preferable for metals with low melting point such as tin and lead, because their confinement in electromagnetic field leads to overheating and fast boiling evaporation, that is not acceptable for nanoparticle synthesis.

Only replacement of inductor, quartz tube and the tube holding heads is required to change flow-levitation mode to the crucible one and back, while all other parts of the equipment, including gas control scheme, pump, electronics etc. remain unchanged.

Depending on the required reaction temperature, either straight tube quartz reactor (reactant input paths 3 or 4), or quartz tube reactor with side reactor input (Figure 1B, reactant input paths 2, higher reaction temperature) may be used both in flow-levitation and in crucible regimes.

Since most of materials in the form of synthesized ultrafine particles are extremely pyrophoric, they need to be passivated by slow in-leakage of atmospheric air (repeatedly, if necessary) before unloading, or poured into a container filled with inert gas.

### 3. Examples of synthesized nanoparticles.

**Table 1.** Examples of metal, alloys and metal compound nanoparticles synthesized using MIGEN equipment.

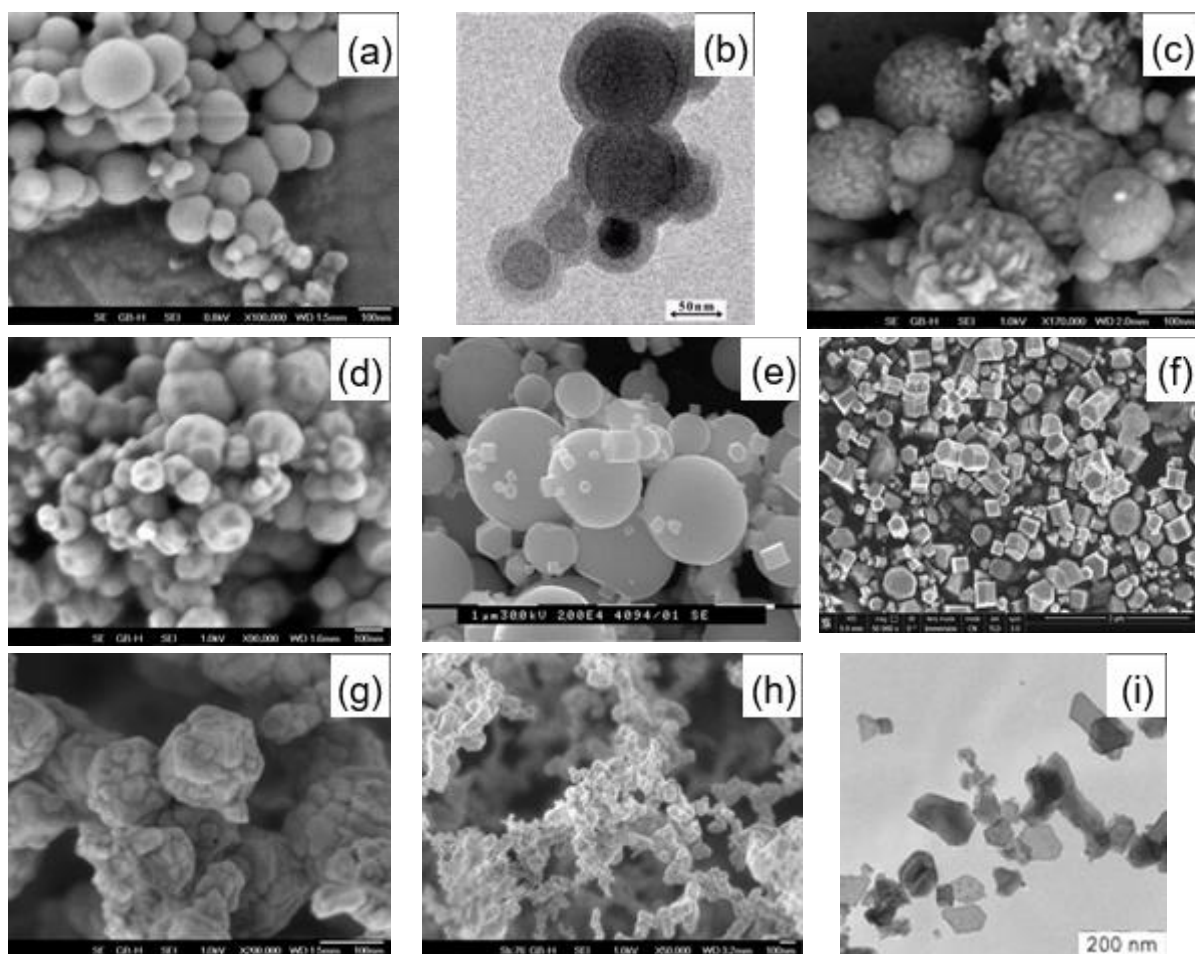
Substance	Particle mean size, nm	Substance	Particle mean size, nm
<b><u>Metals</u></b>		<b><u>Metal compounds</u></b>	
Ag	5-200	Al <sub>2</sub> O <sub>3</sub>	50-150
Co	20-100	NiO	50
Fe	20-100	FeO <sub>x</sub>	50
Zn	170-1400	TiO <sub>x</sub>	15-35
Ti	20-40	TiH <sub>2</sub>	23-30
Al	5-300	Cu <sub>x</sub> O	70
Cu	30-150	CoO	50
Ni	5-100	TiC <sub>x</sub>	15-30
Mn*	80	Fe <sub>x</sub> C	38-45
Mg*	85	TiN <sub>x</sub> , x=0.19-1	15-35
<b><u>Alloys</u></b>		<b><u>Intermetallic compounds</u></b>	
Ni-Cu	40-100	Ni <sub>x</sub> Al	70-120
Fe <sub>x</sub> -Ni <sub>y</sub> -Co <sub>z</sub>	40	Fe-Al	200
Ag-Al	200	Fe-Cu	28-44

\* -- synthesized in crucible regime.



Technical capability of the equipment covers synthesis of nanoparticles of metals with boiling point ranging from some hundreds to approximately 3300 °C with output more than 1 g/h (Table 1).

To manufacture compound or core-shell nanoparticles, practically any desirable gaseous reactant may be used. Liquid reactants with saturation vapor pressure higher than 100 Pa at 20 °C are easy to use for nascent surface chemical treatment. Table 2 presents the examples of reactants and products obtained in nanoparticles synthesis process. Depending on the reactant input conditions (gas pressure, concentration, temperature in the reaction zone), either metal with thin surface coating, or multilayer core-shell structure, or metal compound nanoparticles may be manufactured. Such synthesis influences not only the particles composition, but particle morphology, especially the morphology of the particles surface layer (see figure 3).



**Figure 3.** Electron microscopy images of metal nanoparticles, synthesized via MIGEN equipment:

a) Al, “thin” oxide coating, 18 mm straight tube reactor, mean size  $\langle D \rangle = 85$  nm, mass mean size  $D_m = 131$  nm;

b) Al organic coating (acrylic acid, Path 3), 18 mm straight reactor,  $\langle D \rangle = 72$  nm,  $D_m = 228$  nm;

c) Al “thick” oxide coating, 18 mm reactor, Path 2 side  $O_2$  input,  $\langle D \rangle = 43$  nm,  $D_m = 162$  nm;

d) Al with (oxy)nitride coating 18 mm reactor Path 2 side  $NH_3$  input,  $\langle D \rangle = 93$  nm,  $D_m = 245$  nm;

e) Zn, Ar as carrier gas, 18 mm straight reactor  $\langle D \rangle = 0.72$   $\mu m$ ,  $D_m = 3.91$   $\mu m$ ;

f) Zn,  $H_2 + He$  mixture as carrier gas, 18 mm straight tube reactor  $\langle D \rangle = 206$  nm,  $D_m = 430$  nm;

g) Cu, 18 mm straight tube reactor, reactant ( $Ar + H_2O$  vapor) input through Path 3,  $\langle D \rangle = 86$  nm;

h) Mn, Ar, crucible method, 30 mm straight tube reactor  $\langle D \rangle = 80$  nm,  $D_m = 113$  nm;

i) Mg, Ar, crucible method, 30 mm straight tube reactor,  $\langle D \rangle = 85$  nm,  $D_m = 186$  nm.

**Table 2.** Examples of reactants and products obtained in nanoparticles synthesis process

Reactant	Product
Oxygen	MeO <sub>x</sub> (Me: Ti, Fe, Al, Cu etc.), oxide coating
Dry ammonia	MeN <sub>x</sub> (Me: Ti, Al), (oxy)nitride coating
Hydrocarbons	MeC <sub>x</sub> , C, MeH <sub>x</sub> (Me: Ti, Fe)
Hydrogen	TiH <sub>2</sub>
Carbonic acids	Organic hydrophobic surface coating
Organosilazanes	Silicon-organic hydrophobic surface coating
Perfluoroorganic acids	Fluorine-organic hydrophobic surface coating
Air	Passivating surface coating

**Main technical characteristics of MIGEN equipment.**

Metal wire consumption 1-100 g/h

Power consumption 10 KWt;

Overall size LxBXH = 140X70X200 cm,

Net weight ~ 400 kg.

The equipment automatic control and monitoring system maintains long-term (up to 8 hours) operation without the operator interaction, and is capable to turn itself off in emergency situations.

MIGEN equipment has been delivered and it is currently in use at: The Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, MianYang, and Shenzhou Space Biotechnology Group, China Academy of Space Technology, Beijing, China; Advanced Research Center for Powder Metallurgy and New Materials, Hyderabad, India.

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