REVIEW PAPER

Nanomaterials in Pyrotechnics

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ABSTRACT

Pyrotechnics consist of metallic powders as fuels and different oxidisers which generally have particle size of $> 5 \mu$. The use of nano materials is expected to increase intimate contact between fuel oxidiser, and therefore, development of nano pyrotechnics based on nano fuels oxidizers along with their synthetic routes is considered of great interest. In this review, methods for the preparation of powders of nanometals: aluminium (*Al*), nickel (*Ni*), copper (*Cu*), titanium (*Ti*), iron (*Fe*), silver (*Ag*), and cobalt (*Co*) and; metallic oxides: molybdenum trioxide (MoO_3), tungsten trioxide (WO_3), iron (III) oxide (Fe_2O_3), copper (I) oxide (Cu_2O), antimony trioxide (Sb_2O_3), nickel oxide (*NiO*), manganese dioxide (MnO_2), and zirconium dioxide (ZrO_2) along with their characterisation are discussed. Some nano oxidisers such as $PbCO_3$, $Mg(OH)_2$, NH_4ClO_4, NH_4NO_3 have also been reported. Further, some nano pyrotechnic formulations $Al\text{-}MO_3$, $Al\text{-}WO_3$, $Al\text{-}Fe_2O_3$, *Al*-AP, $Al\text{-}Bi_2O_3$, *Al-CaO* based on nanofuels oxidisers have also been formulated.

Keywords: Nanomaterials, pyrotechnics, nanocomposites, nanometal powders, nanooxidisers

1. INTRODUCTION

Pyrotechnics are mixtures of metal powders and oxidisers. The redox reaction in pyrotechnic formulations is responsible for release of energy in the form of light, sound, and heat. The rate of reaction depends on the particle size of the ingredients and also on their proportions. It is also known that as the particle size decreases, rate of reaction increases, resulting in release of enhanced rate of energy. Thus, nanometal powders and nanooxidisers are expected to give better performance. Due to these advantages, use of such materials in pyrotechnics is increasing day by day.

2. PREPARATION OF NANOMETAL FUELS

The preparation of metallic nanopowders, especially those which readily react with oxygen, is more challenging and some of the methods generally used for their preparation are described.

2.1 Condensation of Metal Vapours

In this method, nanosized metal powders have been produced by the evaporation of coarse metal powders followed by condensation in a radio frequency inductively-coupled plasma and cooling by liquid nitrogen.

2.2 Organometallic Reactions in Non-aqueous Solvents

Organometallic compounds are suspended in an organic solvent and catalytic decomposition is carried out. In case, metal powders are very reactive to oxygen, these are also coated with a suitable material to prevent further oxidation.

Nanometal powders are commercially prepared using the following approaches:

(i) Induction and arc plasmas,

(ii) Vaporisation from molten poll into an inert gas under vacuum, and

(iii) Wire explosion.

The Fig.1 shows TEM images of *Al* nanopowder prepared by different methods[1].

Puszynski[2] synthesised *Al* nanopowder by vapour condensation in a stream of inert gas under vacuum. Metals are inherently reactive to oxygen, and therefore, their surfaces are always covered by oxide layers which have thickness in nano range. A layer of 2–3 nm of oxide, which is generally noncrystalline, is sufficient to minimise further oxidation. The formation of the protective layers on passivated *Al* nanopowder was successfully done using self-assembled nanolayers using perfluoroalkyl carboxylic acid[3]. Other techniques, based on atomic layer deposition were also developed for coating of unpassivated metallic nanopowders[4,5].
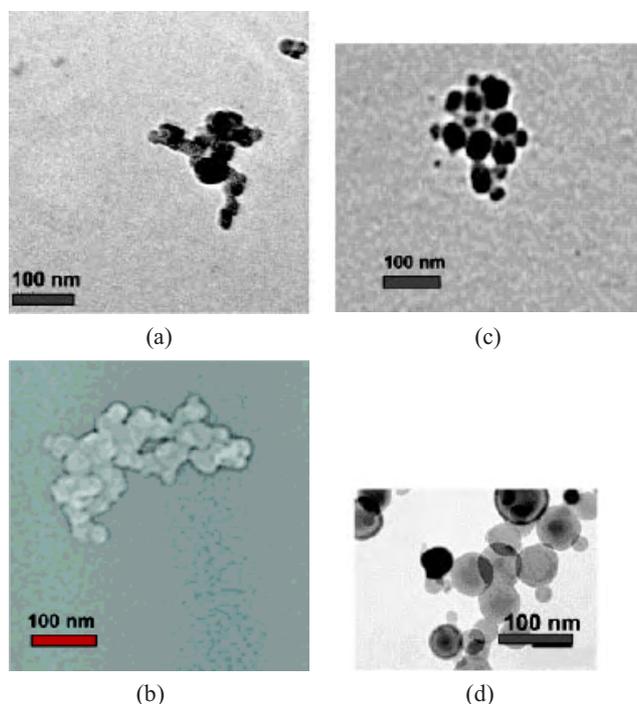

Figure 1. Morphology of *Al* particles prepared by: (a) dc arc, (b) laser ablation, (c) *Al* nanopowder (Aveka Inc), and (d) *Al* nanopowder (Nanotechnologies Inc)[1].

Sandstorm[6], *et al.* synthesised *Al* nanopowder (25–80 nm) by dynamic gas condensation and fully characterised it by different techniques. Jason[7], *et al.* prepared *Al* nanoparticles in solution by catalytic decomposition of H_3AlNMO_3 or $H_3AlN(Me)$ Pyr by $Ti(OPr)_4$ and coated these *in situ* using perfluoroalkyl carboxylic acid. Because *Al* nanoparticles were prepared using wet chemical technique and coated the particles *in situ* in solutions, these were free from oxygen passivation. This self-assembled monolayer (SAM) coating passivates *Al* nanoparticles and prevents their oxidation in air and also renders the composite materials, to some extent, soluble in polar organic solvents, such as diethyl ether.

Ivanov[8], *et al.* presented a new approach for the production of metal powders by exploding wire method and found that the basic factors which govern the quality of metal powders are: (i) level and uniformity of the energy dissipated in this method, (ii) density and chemical reactivity of the surrounding gas, and (iii) initial radius of the wire. The transmmission electron microscopy (TEM) and BET methods were used for their analysis. They produced ultrafine *Al* nanopowder and also metal powders of, *W, Zr, Cu, Fe, Ag, Co, In*, and *Pt* using this technique in the presence of inert gases like N_2, *Ar*, *Xe*, or *He*. Similarly, many researchers also reported preparation of *Ti* metal powder[9-11].

Nickel nanopowder was prepared by chemical reduction methods and particle size was ≈ 50 nm. Also, they have reported preparation of *Ni-B* amorphous nanopowder ≈ 20 nm[12]. Leili[13], *et al.* reported preparation of nano *Ni* (50 nm), nano *Cu* (90 nm), nano *Al* (30 nm), and nano *Ni-Cu* (45 nm) and studied their effect on thermal decomposition of ammonium perchlorate. Nickel and *Cu* nanopowders were prepared from aqueous solution by reducing their corresponding metal salts under suitable conditions[14,15]. Zhang[16], *et al.* reported a new method of preparation in which x-rays were incorporated to get *Ni* nanopowder.

Lithium nanopowder was prepared having particles diameters in the range 5 nm to 30 nm. Similarly, particles of tungsten powder were of spherical form and their diameters were in the range 10–30 nm. Both histograms of size distribution are given by Ivanov[8], *et al.* Besser[17], *et al.* prepared nano *Si* (10

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nm to 100 nm) and scaled up to kg level, using an induction-coupled plasma facility. In this process, coarse powder was vapourised in an hydrogen-argon plasma torch and condensed in a stream of argon. Si[18], *et al.* synthesised amorphous nano *B* particles by the arc decomposition of diborane and the resulting Boron nanopowder had ideal morphology as compared to *B* powders fabricated by furnace or laser heating of diborane.

Amarchand[19], *et al.* prepared *Ti* nanopowder by a novel chemical solution synthetic route from TiO_2. In this method, TiO_2 was allowed to form a complex titanium catecholate precursor, in the presence of ammonium sulphate and concentrated sulphuric acid. The complex was filtered, washed with isopropyl alcohol and dried. On the contrary, titanium hydride was prepared by heating the titanium catecholate precursor at 800 °C in an hydrogen atmosphere. Subsequently, the product was dehydrogenated in 8×10^{-6} torr vacuum to get nanosized titanium powder (≈ 21.6 nm).

3. PREPARATION OF NANOOXIDISERS

Walker[20] developed a modified sol-gel method for Fe_2O_3 xerogels. It allows the design and control of the interfacial area between oxidant (iron oxide matrix) and metal-reducing agent. The modification constituted addition of a new class of di-functional template molecules such as diamines or di-acids as gelation agents. The study of p*H* profile indicated that the mechanism of reactions of propylene oxide and of succinic acid as gelation agents was fundamentally different.

Propylene oxide acts as a proton scavenger, reduces hydrated iron species to Fe_2O_3, and thus reduces the concentration of protons in the reaction mixture, leading to an increase in p*H*. On the other hand, in case of succinic acid as gelation agent, a decrease in p*H* versus time during the reaction indicates formation of carboxylate ions, then creating reactive mols that are capable of stabilising the Fe_2O_3 clusters during the growth process. Ultrafine Fe_2O_3 was prepared through precipitation method by Chen[21], *et al.*

Prakash[22], *et al.* reported sol-gel reactions in the aerosol phase involving iron (III) salt with an epoxide in a volatile solvent (ethanol) to generate porous oxidiser nanoparticles. The porosity of the particles results from the nature of the sol-gel chemical method however, the particle size was in the range 100–230 nm.

Zhu[23], *et al.* reported synthesis of nano Sb_2O_3 by liquid phase homogenous precipitation method with microwave heating in urea which affects particle size considerably. Frolov[24], *et al.* have prepared ammonium nitrate by vacuum evaporation method followed by deposition on a liquid nitrogen-cooled substrate. Ammonium nitrate was deposited over a 90 min process time after evaporation at 1330 °C to give orthorhombic bipyramidal nanocrystals with particle size < 50 nm. Perry[25], *et al.* synthesised nano WO_3 using wet chemical method. In this method, ammonium paratungstate is dissolved in acid followed by precipitation of tungstic acid by the addition of distilled water. The resulting powder was filtered, and dried which is cubic or monoclinic WO_3. Further, WO_2 was made by reducing WO_3 in a stream of H_2 at 650 °C.

Zhu[26], *et al.* synthesised Cu_2O by the precipitation method at room temperature by using $Cu(NO_3)_2$ and $NaOH$ as the starting materials and hydrazine hydrate as a reducing agent. It was noted during the precipitation of Cu_2O that the concentration of the $NaOH$ solution is vital in deciding the shape of the Cu_2O nanocrystals. Needle-shaped Cu_2O nanocrystals with a diameeter of 20 nm are obtained with high concentration of $NaOH$ solution whereas polygonal Cu_2O (40 nm) results with low concentration of $NaOH$. Further, average particle size of the Cu_2O nanocrystals decreases from 68 nm to19 nm with increase in the concentration of $Cu(NO_3)_2$ solution.

Gash[27], *et al.* reported various oxides such as WO_3, *NiO,* and MnO_2 with markedly different particle morphologies. These were prepared by sol-gel method. Figure 2 shows typical structure of MnO_2 and Fig. 3 shows SEM images of iron oxide.

Yanping[28], *et al.* synthesised nano *NiO* by solid state reaction method wherein stoichiometric amounts of $Ni(OAl)_2.4H_2O$ and *NaOH* with appropriate amount of Tween 80 (polyoxyethelene sorbitan monooleate) were ground in an agate mortar at
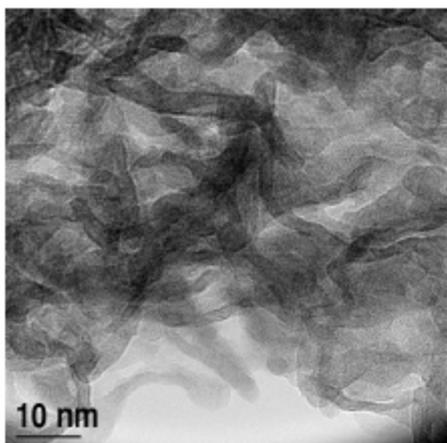
Figure 2. TEM image[27] of sol-gel nanostructured MnO_2.

room temperature for about half an hour. The product was washed with distilled water and absolute ethanol. Then the mixture was treated in ultrasonic bath, centrifuged, and dried in a desiccator at 80 °C for 4 h. Light green powder was sintered at 40 °C for 2 h to get ~10 nm NiO nanoparticles.

Using solid state reaction of $CoCl_2.6H_2O$ with $NaOH$, $H_2C_2O_4.2H_2O$, $Na_2CO_3.10H_2O$ and $Na_2C_2O_4$ in different particle sizes, Weifen[29], *et al.* prepared Co_3O_4 at room temperature. The resulting Co_3O_4 powders had particle sizes 23 nm, 30 nm, 35 nm, and 150 nm, respectively.

4. PYROTECHNIC FORMULATIONS

Walter[30], *et al.* reported a thermite composition $Al–MoO_3$ with Al nanopowder (30–90 nm) and O/F ratio as 1:4. The burning rate study of this formulation indicated that the surface area of MoO_3 affected the burning rate which was decreases when surface area was decreases from 64–40 m²/g.

On aging, it was also observed that MoO_3 decreases its surface area two-folds within 10–12 days. Nanostructured aerogel and xerogel formulations of sol-gel iron (III) oxide and ultrafine grained Al (M/S UFG) were prepared[31].

Using nanostructured hydrocarbon resin fuel network and fine NH_4ClO_4 the pyrotechnic formulation was prepared. Schoenitiz[32], *et al.* prepared Al-Fe_2O_3 and Al-MoO_3 by asserted reactive milling (ARM) with high energy and the particle sizes of the resulting powders could be varied by changing milling parameters. Ignition/combustion behaviour of nanocomposites Al-MoO_3 was reported by Granier[33], *et al.* The pellets formulations consisting of nano reactant particles, mixed and pressure-moulded, to get 49.73 per cent of the theoretical maximum density (TMD), were prepared. Ignition sensitivity was determined by measuring the ignition delay time and temperature by using a 50 W CO_2 laser and thermocouples, respectively. Using high speed camera and recording system, the speed of the combustion waves was measured.

Guang[23], *et al.* prepared $Al–WO_x$ stoichiometric mixes and measured burning rate in open tray and it was found to be 2.5 m/s. Bockman[34], *et al.* formulated $Al–MoO_3$ composites and studied their physiochemical properties. The composites studied contained tailored ultrafine grain Al (30–200 nm) particles that dramatically increase of the rate of energy release of these thermite formulations. Moore[35], *et al.* carried out emission spectroscopy of $Al–MoO_3$ (both of nanosize) formulations and reported flame temperature of the order of 3200 K. The intensity of AlO species were observed to change with the ratio of $Al–MoO_3$.
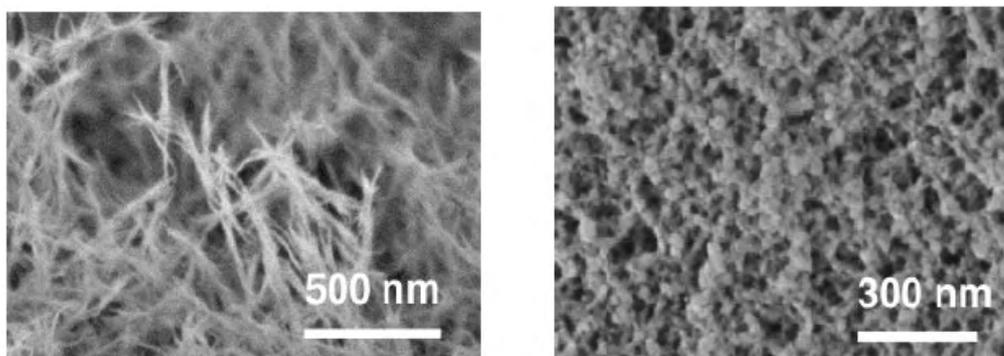

Figure 3. SEM images of two iron (III) oxides obtained by sol-gel[27] method.

Bulian[36], *et al.* studied ignition of nanopowder *Al* with MoO_3, WO_3, Bi_2O_3, and CuO by DSC and concluded that Bi_2O_3 and CuO oxides possess high reactivity than other oxides. The effect of particle size and reactant coatings and ageing of individual *Al* powders on burning rate velocities was also studied.

Plantier[37], *et al.* studied the effect on burning characteristics of Fe_2O_3 prepared by sol-gel process and commercially available nano Fe_2O_3. Nano *Al* powder (52 nm) was mixed in different proportions with Fe_2O_3 and the burn rates were compared and an equivalence of 1 : 4 provided an optimum burn-rate regardless of synthetic technique used for oxidisers. The data on combustion and explosive characteristics of binary mixtures of nano *Al* (Alex) with NH_4ClO_4, $KClO_4$, KNO_3, and $NaNO_3$ were given by Ivanov[38], *et al.*

Prakash[39], *et al.* reported a new metastable intermolecular composite based on $Al–KMnO_4$ which had faster reaction rate than the known formulations such as $Al–CuO$ and $Al–MoO_3$. The $KMnO_4$ nanoparticles were synthesised by spray-drying method. Using a 5 Wt per cent aquous solution of $KMnO_4$ droplets of the precursor solution of about 1 μm geometric mean diameter were generated using a collision-type atomiser. The moisture from the aerosol was absorbed is a silica-gel diffusion dryer, following which the aerosol was passed through a tube furnace maintained at 150 ºC to vapourise the remaining moisture. The residence time of the aerosol in the furnace was about 1 s for a nominal flow rate of 3 l min^{-1}. Nanoparticles of $KMnO_4$ of 250 nm mean diameter were collected on 0.6 μm filter manufactured by Millipore (filter code DTTP).

Yang[40], *et al.* synthesised $NiO–Al$ composite at the nano level in which NiO had particle size of 12 nm. Nano *Al* with WO_3, MoO_3, CuO, and Fe_2O_3 formulations were also prepared by Valliappans[41], *et al.* who concluded that the combustion front velocity in $Al–CuO$ was strongly affected by the presence of surface functional coatings. Nano $Si–KClO_4$ formulations were also studied for combustion velocity[17]. Aluminium and *Ta* metal nanopowders were used to prepare pyrotechnic formulations with Bi_2O_3 as an oxidiser and their impact sensitivity was studied using a lab gas gun[42]. A new approach was developed by self-assembly fuel nanoparticles around an oxidiser matrix using a mono Functional polymer, poly(4)–vinyl pyridine. The polymer was used to accomplish binding of fuel and oxidiser particles in a molecularly -engineered manner, where $Al–CuO$ composite gave higher burning rates[43].

Ramaswamy[44], *et al.* reported the use of nanometal particles and CNTs as an encapsulator to nanoparticles of explosives and oxidisers which are used for the incorporation in novel formulations for weaponisation purposes.

Prantice[45], *et al.* synthesised a nanocomposite of a ternary thermite containing $Al–Fe_2O_3–SiO_2$ (using sol-gel processing technique) and other formulations by a physical mixture of discrete
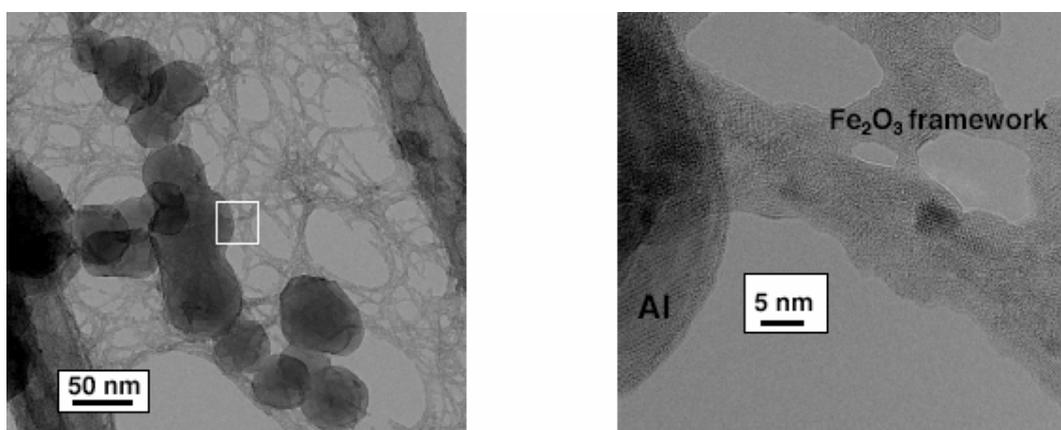

Figure 4. TEM of sol-gel $Fe_2O_3–Al$ nanocomposite.

nanoparticles. The burning rate of the composite was 40 m/s as compared to physically prepared mixture at 9 m/s. Figure 4 shows TEM of nanocomposite[27] of Fe_2O_3 and Al.

Clapsaddle[46], *et al*. synthesised Fe_2O_3–SiO_2 and Fe_2O_3–SiO_2 –R oxides [R=$(CH_2)_2$ $(CF_2)_7CF_3$] using sol-gel techniques. The subsequent energetic nanoformulations were prepared by physically mixing fuel and nanooxidisers. The fuel and oxidisers were suspended in 60 ml of hexane. The mixtures were sonicated and then evaporated. Two formulations reported are:

Fomulation A   : Thermite Al–Fe_2O_3 . SiO_2
Formulation B : Gas generator Al–Fe_2O_3 .SiO_2–R
                       [R = $(CH_2)_2$ $(CF_2)_7$ .CF_3]

In this, formulation A worked as thermite while formulation B as gas generator. In the case of silica composites, use of burning rate modifiers allowed control of reaction rate and energy output which were based on the method of synthesis and amount of burn-rate modifier.

Menon[47], *et al*. reported the creation of iron oxide nanowire arrays (oxidiser) placed in contact with an aluminium film (fuel). A schematic illustration of the approach developed for the fabrication of such nanocomposites in the laboratory is shown in Fig. 5.

The detailed procedure is described in the literature. The ignition of nanocomposites was achieved using butane flame, resistive heating wire, and laser illumination and flame temperature was found to be around 4000 °C.

5. OTHER NANOSIZED MATERIALS

Chen[48], *et al*. synthesised nano $PbCO_3$ by mixing $Pb(CH_3COO)_2.3H_2O$ and Na_2CO_3 in 8000 rpm fast mixing equipment. The nanoparticles showed narrow size distribution and particle size was in the range 10–30 nm.

Qing[49], *et al*. reported nano $PbCO_3$ using modified chemical precipitation method and found orthorhombic crystals with uniform spherical particles of 50 nm. Nano $Mg(OH)_2$,which was synthesised by high gravity method, had particle size of about 70 nm as reported
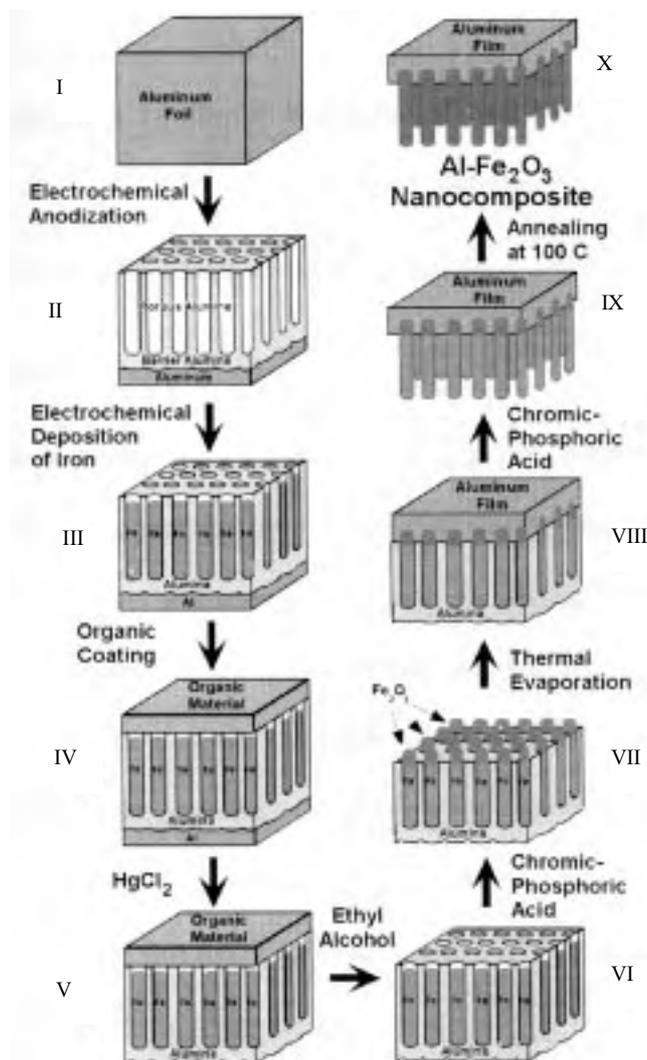

Figure 5. Approach for the fabrication of nanocomposites.

by Song[50], *et al*. and its surface was modified by coating with polyvinyl chloride.

6. CONCLUSIONS

The preparation of nanometal powders is a very complex procedure but their development is essential to meet the requirements of futuristic missions. Metal powders like Mg, Al, Zr, W, B, Ni, etc are widely used in formulations and have been prepared in nanosize on a laboratory scale except nano Al which is commercially available. The oxidisers like metal chlorates, perchlorates, nitrates, chromates, etc are also used in pyrotechnic formulations but efforts have not been made to produce these on a nanoscale. As these materials will be required in bulk, there is a need to scale up their methods of preparation.

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