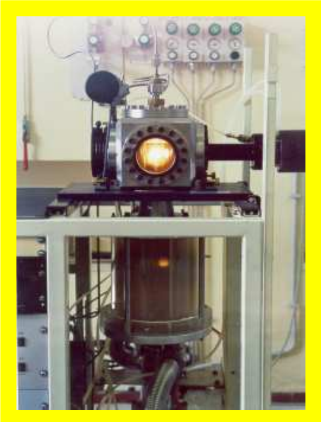
Laser synthesis of nanoparticles: from ceramic nanocomposites to nanofluids

Nanoparticles (NPs) are the starting point of many approaches for realizing nanostructured materials and devices, hence their synthesis is a critical part of the rocketing research effort in nanoscale science. To date, the production of large amounts of pure, non-agglomerated NPs, with desired size and narrow size distribution, results to be an extremely difficult task. To this respect, the technique of laser pyrolysis of gas-phase reactants appears as a very flexible tool for the synthesis of a variety of NPs in developmental quantities. In this approach, heating of the vapour phase mixture is obtained by use of a CO_2 laser (10.6 µm), whose energy is absorbed by at least one of the precursors introduced into the reaction chamber or by an inert photosensitizer. The high



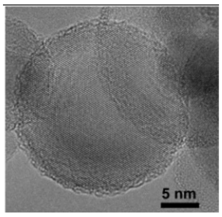
power of the laser induces considerable light absorption, leading to a rapid increase of the temperature in the gas. The resulting effects are the rapid energy thermalization by collisional transfer and the dissociation of reactants. Once nucleation occurs, growth of NPs takes place in a very short time by coagulation and coalescence of the reaction products, abruptly terminated as soon as the NPs leave the irradiation region. Solid products are NPs with average size in the range 5-30 nm and a narrow size distribution. Recently, the ENEA laser pyrolysis facility was equipped with an evaporator for using liquid precursors in order to increase the range of compositions of the produced NPs.

In the following, an overview will be given on the properties and applications of the innovative materials for structural and functional applications that are prepared at ENEA starting from pyrolytic NPs.

Nanopowders have long been investigated as a useful reinforcement material to improve the thermomechanical properties of structural ceramic composites. To this purpose, Si-based NPs (SiC and Si_3N_4) can be synthesized by laser pyrolysis of SiH_4 in the presence of C_2H_2 and NH_3, respectively. Various nanocomposites (Al_2O_3/SiC, Si_3N_4/SiC etc..) have been fabricated, especially by hot pressing, however until now not any unquestionable beneficial effect on the mechanical properties has been found. This is likely due to microstructural inhomogeneities like NPs aggregates, microcracks and pores producing critical defects in the dense composite. On the other hand, full exploitation of the properties of pyrolytic NPs can be attained in applications were the sensitivity to the defect population is not so critical (like erosion/corrosion protective coatings) and/or specific

functions are required (optical, magnetic etc..).
In fact corrosion and wear resistant composite coatings have been realized by electrochemical co-deposition of ENEA SiC NPs with different matrix materials (nickel or bronze) on steel

substrates. Moreover, an improvement is observed in the mechanical properties of fibre reinforced ceramic-matrix composites (CMCs) prepared by electrophoretic infiltration of carbon fibres fabrics with suspensions of ENEA pyrolitic SiC nanopowders.



In recent years, a huge effort has being dedicated to the synthesis and functionalization of Si NPs to enhance and control their optical emission properties. In this framework, the infrared PL (Photo-Luminescence) emitted from pyrolytic Si NPs can find interesting applications in the field of bio-imaging. As prepared Si NPs, however, exhibit weak or even no emission. The PL intensity increases as a result of (noncontrollable) exposure to air, passivation in liquids, or ad-hoc (soft) wet-oxidation processing of pristine NPs. In order to exploit the potential for bio-medical applications, Si NPs should remain highly luminescent and well dispersed in water and biological fluids over a wide range of pH and salt concentrations. Moreover, for in vitro and in vivo applications, NPs should be coated with a biocompatible polymer to prevent the formation of large aggregates and to improve biodistribution. In the course of the EC BONSAI Project, colloidally stable and biocompatible Si NPs were obtained by grafting hydrophilic polymer chains, such as poly(ethylene glycol), on the NPs surfaces.

Another set of applications was driven by the observation that optically excited Si nanocrystals are very effective in transferring energy to nearby rare earth-ions. This property is explored for applications ranging from the realization of Er-doped planar optical amplifiers to the preparation of biomarkers with optical emission more stable and tunable over a wider range of wavelengths than the PL emitted from Si nanocrystals. For example, emission at 980 nm from Yb doped Si NPs was observed upon optical excitation in the absorption band of Si NPs.

Use of liquid precursors has made possible the preparation of considerable quantities (hundreds of grams) of nano-TiO_2 and -SiO_2 that are used for the preparation of nanofluids with enhanced heat exchange properties, in the framework of the EC Project FP7-NanoHex. Nanofluid coolants are expected to have a strong impact in industrial heat management. Samples of TiO_2 and SiO_2 are produced by laser pyrolysis of titanium tetraisopropoxide and tetraethyloxisilane, respectively. In both cases, C_2H_4 is employed as reaction sensitizer. An enhancement in the thermal conductivity (with respect to distilled water) was observed at the University of Birmingham in all the nanofluids based on TiO_2 and SiO_2 and SiC pyrolytic NPs in water. Thermal tests on nanofluids are in progress.

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