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Nanocomposite Science and Technology

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Preface

The field of nanocomposites involves the study of multiphase material where at least one of the constituent phases has one dimension less than 100 nm. The promise of nanocomposites lies in their multifunctionality, the possibility of realizing unique combinations of properties unachievable with traditional materials. The challenges in reaching this promise are tremendous. They include control over the distribution in size and dispersion of the nanosize constituents, tailoring and understanding the role of interfaces between structurally or chemically dissimilar phases on bulk properties. Large scale and controlled processing of many nanomaterials has yet to be achieved. Our mentor as we make progress down this road is mother Nature and her quintessential nanocomposite structures, for example, bone.

We realize that a book on a subject of such wide scope is a challenging endeavour. The recent explosion of research in this area introduces another practical limitation. What is written here should be read from the perspective of a dynamic and emerging field of science and technology. Rather than covering the entire spectrum of nanocomposite science and technology, we have picked three areas that provide the basic concepts and generic examples that define the overall nature of the field. In the first chapter we discuss nanocomposites based on inorganic materials and their applications. In the second chapter polymer based nanoparticle filled composites are detailed with an emphasis on interface engineering to obtain nanocomposites with optimum performance. The third chapter is about naturally occurring systems of nanocomposites and current steps towards naturally inspired synthetic nanocomposites. Finally a short chapter contributed by our colleagues highlights the possibility of using theoretical models and simulations for understanding nanocomposite properties. We hope our readers will find the book of value to further their research interests in this fascinating and fast evolving area of nanocomposites.

Troy, July 2003   *P. M. Ajayan, L. S. Schadler and P. V. Braun*

1
Bulk Metal and Ceramics Nanocomposites

Pulickel Ajayan

1.1
Introduction

The field of nanocomposite materials has had the attention, imagination, and close scrutiny of scientists and engineers in recent years. This scrutiny results from the simple premise that using building blocks with dimensions in the nanosize range makes it possible to design and create new materials with unprecedented flexibility and improvements in their physical properties. This ability to tailor composites by using nanosize building blocks of heterogeneous chemical species has been demonstrated in several interdisciplinary fields. The most convincing examples of such designs are naturally occurring structures such as bone, which is a hierarchical nanocomposite built from ceramic tablets and organic binders. Because the constituents of a nanocomposite have different structures and compositions and hence properties, they serve various functions. Thus, the materials built from them can be multifunctional. Taking some clues from nature and based on the demands that emerging technologies put on building new materials that can satisfy several functions at the same time for many applications, scientists have been devising synthetic strategies for producing nanocomposites. These strategies have clear advantages over those used to produce homogeneous large-grained materials. Behind the push for nanocomposites is the fact that they offer useful new properties compared to conventional materials.

The concept of enhancing properties and improving characteristics of materials through the creation of multiple-phase nanocomposites is not recent. The idea has been practiced ever since civilization started and humanity began producing more efficient materials for functional purposes. In addition to the large variety of nanocomposites found in nature and in living beings (such as bone), which is the focus of chapter 3 of this book, an excellent example of the use of synthetic nanocomposites in antiquity is the recent discovery of the constitution of Mayan paintings developed in the Mesoamericas. State-of-the-art characterization of these painting samples reveals that the structure of the paints consisted of a matrix of clay mixed with organic colorant (indigo) molecules. They also contained inclusions of metal nanoparticles encapsulated in an amorphous silicate substrate, with oxide nanoparticles on the substrate

[1]. The nanoparticles were formed during heat treatment from impurities (Fe, Mn, Cr) present in the raw materials such as clays, but their content and size influenced the optical properties of the final paint. The combination of intercalated clay forming a superlattice in conjunction with metallic and oxide nanoparticles supported on the amorphous substrate made this paint one of the earliest synthetic materials resembling modern functional nanocomposites.

Nanocomposites can be considered solid structures with nanometer-scale dimensional repeat distances between the different phases that constitute the structure. These materials typically consist of an inorganic (host) solid containing an organic component or vice versa. Or they can consist of two or more inorganic/organic phases in some combinatorial form with the constraint that at least one of the phases or features be in the nanosize. Extreme examples of nanocomposites can be porous media, colloids, gels, and copolymers. In this book, however, we focus on the core concept of nanocomposite materials, i.e., a combination of nano-dimensional phases with distinct differences in structure, chemistry, and properties. One could think of the nanostructured phases present in nanocomposites as zero-dimensional (e.g., embedded clusters), 1D (one-dimensional; e.g., nanotubes), 2D (nanoscale coatings), and 3D (embedded networks). In general, nanocomposite materials can demonstrate different mechanical, electrical, optical, electrochemical, catalytic, and structural properties than those of each individual component. The multifunctional behavior for any specific property of the material is often more than the sum of the individual components.

Both simple and complex approaches to creating nanocomposite structures exist. A practical dual-phase nanocomposite system, such as supported catalysts used in heterogeneous catalysis (metal nanoparticles placed on ceramic supports), can be prepared simply by evaporation of metal onto chosen substrates or dispersal through solvent chemistry. On the other hand, material such as bone, which has a complex hierarchical structure with coexisting ceramic and polymeric phases, is difficult to duplicate entirely by existing synthesis techniques. The methods used in the preparation of nanocomposites range from chemical means to vapor phase deposition.

Apart from the properties of individual components in a nanocomposite, *interfaces* play an important role in enhancing or limiting the overall properties of the system. Due to the high surface area of nanostructures, nanocomposites present many interfaces between the constituent intermixed phases. Special properties of nanocomposite materials often arise from interaction of its phases at the interfaces. An excellent example of this phenomenon is the mechanical behavior of nanotube-filled polymer composites. Although adding nanotubes could conceivably improve the strength of polymers (due to the superior mechanical properties of the nanotubes), a noninteracting interface serves only to create weak regions in the composite, resulting in no enhancement of its mechanical properties (detailed in chapter 2). In contrast to nanocomposite materials, the interfaces in conventional composites constitute a much smaller volume fraction of the bulk material.

In the following sections of this chapter, we describe some examples of metal/ceramic nanocomposite systems that have become subjects of intense study in recent years. The various physical properties that can be tailored in these systems for specific

applications is also considered, along with different approaches to synthesizing these nanocomposites.

1.2
Ceramic/Metal Nanocomposites

Many efforts are under way to develop high-performance ceramics that have promise for engineering applications such as highly efficient gas turbines, aerospace materials, automobiles, etc. Even the best processed ceramic materials used in applications pose many unsolved problems; among them, relatively low fracture toughness and strength, degradation of mechanical properties at high temperatures, and poor resistance to creep, fatigue, and thermal shock. Attempts to solve these problems have involved incorporating second phases such as particulates, platelets, whiskers, and fibers in the micron-size range at the matrix grain boundaries. However, results have been generally disappointing when micron-size fillers are used to achieve these goals. Recently the concept of nanocomposites has been considered, which is based on passive control of the microstructures by incorporating nanometer-size second-phase dispersions into ceramic matrices [2]. The dispersions can be characterized as either
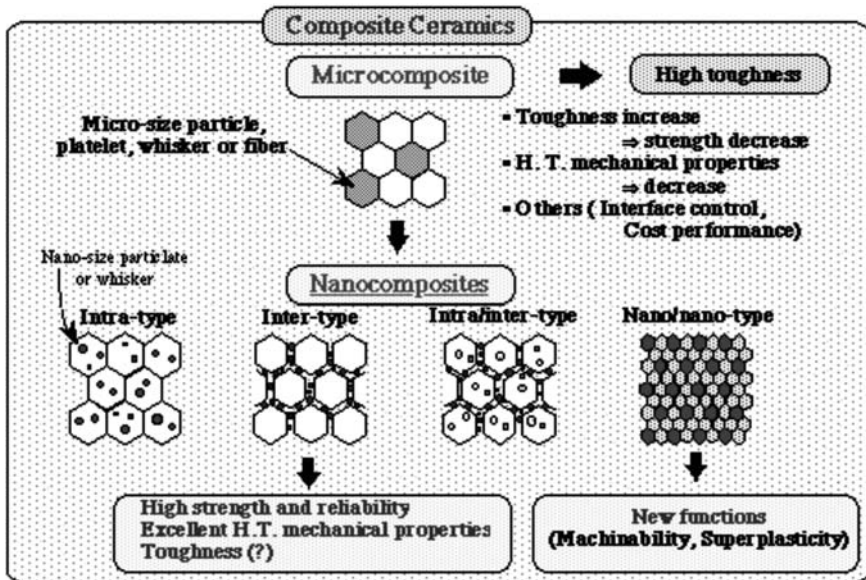
Fig. 1.1 New concept of ceramic metal nanocomposites with inter- and intra-granular designs: properties of ceramic materials can be improved by nanocomposite technology. This technique is based on passive control of the microstructures by incorporating nanometer-sized second dispersions into ceramic materials. This is a completely new method to fabricate materials with excellent mechanical properties (such as high strength and toughness), due to the desirable microstructure of ceramics (Source:[228] Reprinted with permission)

intragranular or intergranular (Figure 1.1). These materials can be produced by incorporating a very small amount of additive into a ceramic matrix. The additive segregates at the grain boundary with a gradient concentration or precipitates as molecular or cluster sized particles within the grains or at the grain boundaries. Optimized processing can lead to excellent structural control at the molecular level in most nanocomposite materials. Intragranular dispersions aim to generate and fix dislocations during the processing, annealing, cooling, and/or the in-situ control of size and shape of matrix grains. This role of dispersoids, especially on the nano scale, is important in oxide ceramics, some of which become ductile at high temperatures. The intergranular nanodispersoids must play important roles in control of the grain boundary structure of oxide (Al_2O_3, MgO) and nonoxide (Si_3N_4, SiC) ceramics, which improves their high-temperature mechanical properties [3–6]. The design concept of nanocomposites can be applied to ceramic/metal, metal/ceramic, and polymer/ceramic composite systems.

Dispersing metallic second-phase particles into ceramics improves their mechanical properties (e.g., fracture toughness). A wide variety of properties, including magnetic, electric, and optical properties, can also be, tailored in the composites due to the size effect of nanosized metal dispersions, as described later in the chapter. Conventional powder metallurgical methods and solution chemical processes like sol–gel and coprecipitation methods have been used to prepare composite powders for ceramic/metal nanocomposites such as Al_2O_3/W, Mo, Ni, Cu, Co, Fe; ZrO_2/Ni, Mo; MgO/Fe, Co, Ni; and so on. The powders are sintered in a reductive atmosphere to give homogeneous dispersions of metallic particles within the ceramic matrices. Fracture strength, toughness, and/or hardness are enhanced due to microstructural refinement by the nanodispersions and their plasticity. For transition metal particle dispersed oxide ceramic composites, ferromagnetism is a value-added supplement to the excellent mechanical properties of the composites [7,8]. In addition, good magnetic response to applied stress was found in these ceramic/ferromagnetic-metal nanocomposites, allowing the possibility of remote sensing of initiation of fractures or deformations in ceramic materials.

Nanocomposite technology is also applicable to functional ceramics such as ferroelectric, piezoelectric, varistor, and ion-conducting materials. Incorporating a small amount of ceramic or metallic nanoparticles into $BaTiO_3$, ZnO, or cubic ZrO_2 can significantly improve their mechanical strength, hardness, and toughness, which are very important in creating highly reliable electric devices operating in severe environmental conditions [9]. In addition, dispersing conducting metallic nanoparticles or nanowires can enhance the electrical properties, as described later. Dispersion of soft materials into a hard ceramic generally decreases its mechanical properties (e.g., hardness). However, in nanocomposites, soft materials added to several kinds of ceramics can improve their mechanical properties. For example, adding hexagonal boron nitride to silicon nitride ceramic can enhance its fracture strength not only at room temperature but also at very high temperatures up to 1500 °C. In addition, some of these nanocomposite materials exhibit superior thermal shock resistance and machinability because of the characteristic plasticity of one of the phases and the interface regions between that phase and the hard ceramic matrices.

Advanced bulk ceramic materials that can withstand high temperatures ($>1500\,^\circ$C) without degradation or oxidation are needed for applications such as structural parts of motor engines, gas turbines, catalytic heat exchangers, and combustion systems. Such hard, high-temperature stable, oxidation-resistant ceramic composites and coatings are also in demand for aircraft and spacecraft applications. Silicon nitride (Si_3N_4) and silicon carbide/silicon nitride (SiC/Si_3N_4) composites perform best in adverse high-temperature oxidizing conditions. Commercial Si_3N_4 can be used up to $\sim$1200$\,^\circ$C, but the composites can withstand much higher temperatures. Such Nanocomposites are optimally produced from amorphous silicon carbonitride (obtained by the pyrolysis of compacted polyhydridomethylsilazane $[CH_3SiH\text{-}NH]_m[(CH_3)_2Si\text{-}NH]_n$ at about 1000$\,^\circ$C), which produces crystallites of microcrystals of Si_3N_4 and nanocrystals of SiC [10] (Figure 1.2). The oxidation resistance, determined by TGA analysis, arises from the formation of a thin (few microns) silicon oxide layer.

Processing is key to the fabrication of nanocomposites with optimized properties. Some examples of commonly used processes for creating nanocomposites are discussed below.
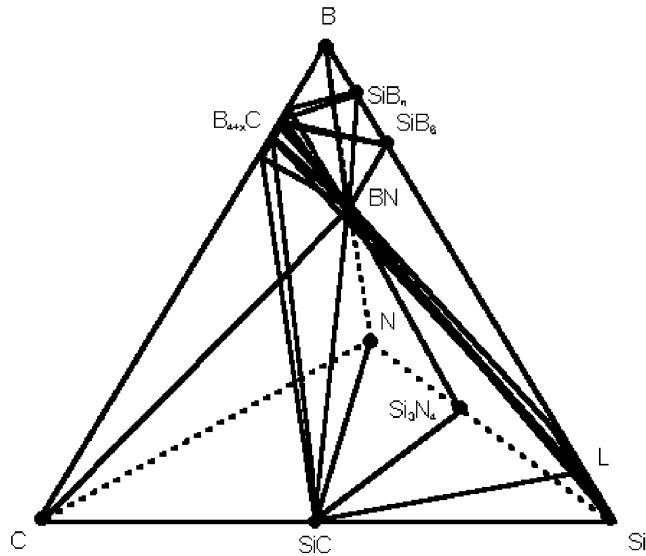
Fig. 1.2 Calculated phase diagrams of the system Si/B/C/N allows for the creation of high-temperature ceramic nanocomposites. The system Si/B/C/N is being investigated with respect to processing new covalent materials. Based on this system, several nanocomposites (SiC/Si$_3$N$_4$) have been developed that can, for example, withstand high temperatures ($\sim$1500$\,^\circ$C) without degradation or oxidation [10]. (Source [229] used with permission) alternative web site: http://aldix.mpi-stuttgart.mpg.de/E_head.html, used with permission

1.2.1
Nanocomposites by Mechanical Alloying

Mechanical alloying was originally invented to form small-particle (oxide, carbide, etc.) dispersion-strengthened metallic alloys (Figure 1.3) [11]. In this high-energy ball milling process, alloying occurs as a result of repeated breaking up and joining (welding) of the component particles. The process can prepare highly metastable structures such as amorphous alloys and nanocomposite structures with high flexibility. Scaling up of synthesized materials to industrial quantities is easily achieved in this process, but purity and homogeneity of the structures produced remains a challenge. In addition to erosion and agglomeration, high-energy milling can provoke chemical reactions that are induced by the transfer of mechanical energy, which can influence the milling process and the properties of the product. This idea is used to prepare magnetic oxide-metal nanocomposites via mechanically induced displacement reactions between a metal oxide and a more reactive metal [12,13]. High-energy ball milling can also induce chemical changes in nonmetallurgical systems, including silicates, minerals, ferrites, ceramics, and organic compounds. The interest in mechanical alloying as a method to produce nanocrystalline materials is due to the simplicity of the method and the possibility for scaled-up manufacturing.

Displacement reactions between a metal oxide and a more reactive metal can be induced by ball milling [14]. The reaction may progress gradually, producing a nanocomposite powder. In some cases, the reaction progresses gradually, and a metal/metal-oxide nanocomposite is formed. Milling may also initiate a self-propagating com-

Fig. 1.3 Schematic of the formation process of typical nanocomposite microstructures by the mechanical alloying method. (Source [230, 11] used with permission)
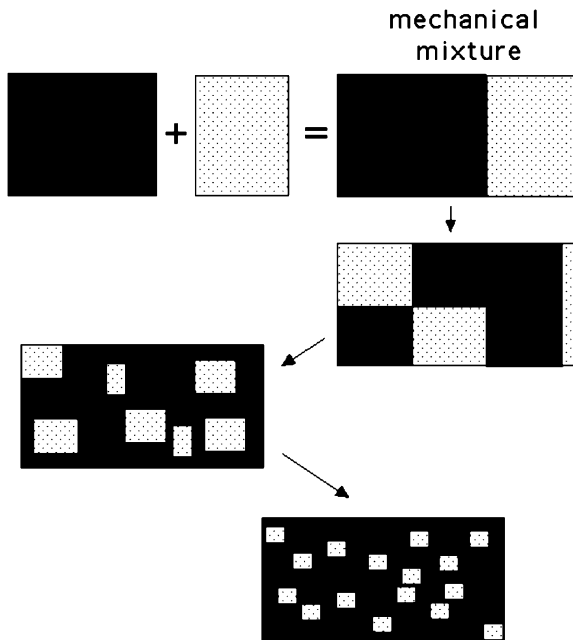
bustive reaction [15]. The nature of such reactions depends on thermodynamic para-
meters, the microstructure of the reaction mixture, and the way the microstructure
develops during the milling process. The mechanical stresses developed during
high impact hits can also initiate combustion in highly exothermic systems, melting
the reaction mixture and destroying the ultrafine (nanocrystalline) microstructure.
Milling mixtures of ceramic and metal powders can induce mechanochemical reac-
tions, and this process is an efficient way of producing nanocermets [16]. Depending
on the thermodynamics of the metal/metal-oxide systems and the kinetics of the ex-
change (displacement) reactions during processing, various nanocomposite systems
could evolve. As an example, the reduction of metal oxides with aluminum during
reactive ball milling can result in nanocomposites of Al_2O_3 and metallic alloys (Fe,
Ni, Cr; particularly binary alloy systems), and such ceramics with ductile metal inclu-
sions produce toughened materials with superior mechanical properties [17]. These
nanocomposite materials also have better thermomechanical properties, such as high-
er thermal shock resistance, due to better metal–ceramic interfacial strength.

   Ball milling by direct milling of a mixture of iron and alumina powders has been
used to prepare nanocomposites with magnetic phases, such as nanoparticles of iron
embedded in an insulating alumina matrix [18]. The average particle size can be re-
duced to the 10-nm range, as indicated by x-ray diffraction linewidths and electron
microscopy. The magnetic properties of this system (e.g., saturation magnetization
and coercivity) can be tailored by changing the phase composition, particle size,
and the internal stresses accumulated during milling. In this system, the iron nano-
particles were formed with lattice strains of about 0.005; coercivities up to 400 Oe were
achieved. The magnetization of the iron particles is 25 % – 40 % less than that expected
for bulk iron. Systems of smaller magnetic particles embedded in a nonmagnetic ma-
trix can be prepared by high-energy ball milling [19]. For example, nanocomposites of
Fe_3O_4 particles dispersed in Cu have been prepared by ball milling a mixture of Fe_3O_4
and Cu powders directly, as well as by enhanced ball milling-induced reaction between
CuO and metallic iron [20]. Both processes result in magnetic semi-hard nanocom-
posites with a significant superparamagnetic fraction, due to the very small particle
sizes of the dispersed magnetic phase. In situ chemical reactions provide a means to
control the ball milling process and to influence the microstructure and magnetic
properties of the product. Nanocomposite magnets (such as hard magnetic SmCoFe
phases in soft magnetic Fe/Co systems), discussed in detail later in this chapter, are
routinely prepared by mechanical milling and heat treatment. The metastable nano-
crystalline/amorphous structures inherently obtained in mechanically alloyed pow-
ders result from repeated deformation and fracture events during collisions of pow-
ders with the balls. Plastic deformation in powders initially occurs through the forma-
tion of shear bands, and when high dislocation densities are reached, the shear bands
degenerate into randomly oriented subgrains. The large surface area of the nanocrys-
talline grains often helps in the transformation of crystalline into amorphous struc-
tures [21]. Deformation-induced defect density and the local changes in temperature
due to impacts affect the diffusion coefficients of the several species involved during
the milling process. In fact, the final microstructure and stoichiometry of mechanically
milled samples often reflects the competing processes of milling-induced disorder and

diffusion-limited recovery, rather than being solely dependent on the starting material (e.g., depending on whether the starting mixtures are pre-alloyed or in their elemental forms).

1.2.2
Nanocomposites from Sol–Gel Synthesis

Aerogels, due to their high-porosity structure, are clearly an ideal starting material for use in nanocomposites. Aerogels are made by sol–gel [22,23] polymerization of selected silica, alumina, or resorcinol-formaldehyde monomers in solution and are extremely light (densities ~$0.5-0.001$ g cc^{-1}) but highly porous, having nanosize pores. In nanocomposites derived from aerogels, the product consists of a 'substrate' (e.g., silica aerogel) and one or more additional phases (of any composition or scale). In the composites, there is always at least one phase whose physical structures have dimensions on the order of nanometers (the particles and pores of the aerogel). The additional phases may also have nanoscale dimensions or may be larger. The systems most commonly made are silica-based nanocomposite systems [24], but this approach can be extended to other aerogel (alumina, etc.) precursors.

Aerogel nanocomposites can be fabricated in various ways, depending on when the second phase is introduced into the aerogel material. The second component can be added during the sol–gel processing of the material (before supercritical drying). It can also be added through the vapor phase (after supercritical drying), or chemical modification of the aerogel backbone may be effected through reactive gas treatment. These general approaches can produce many varieties of composites. A non-silica material is added to the silica sol before gelation. The added material may be a soluble organic or inorganic compound, insoluble powder, polymer, biomaterial, etc. The additional components must withstand the subsequent processing steps used to form the aerogel (alcohol soaking and supercritical drying). The conditions encountered in the CO_2 drying process are milder than in the alcohol drying process and are more amenable to forming composites. If the added components are bulk insoluble materials, steps must be taken to prevent its settling before gelation. The addition of soluble inorganic or organic compounds to the sol provides a virtually unlimited number of possible composites. Two criteria must be met to prepare a composite by this route. First, the added component must not interfere with the gelation chemistry of the aerogel precursor. Possible interference is difficult to predict in advance, but it is rarely a problem if the added component is reasonably inert. The second problem is the leaching out of the added phases during the alcohol soak or supercritical drying steps. This problem can be a significant impediment if a high loading of the second phase is desired in the final composite. When the added component is a metal complex, it is often useful to use a chemical binding agent that can bind to the silica backbone and chelate the metal complex. Many use this method to prepare nanocomposites of silica aerogels or xerogels. After the gel is dried, the resulting nanocomposite consists of an aerogel with metal atoms or ions uniformly (atomically) dispersed throughout the material. Thermal post-processing creates nanosize metal par-
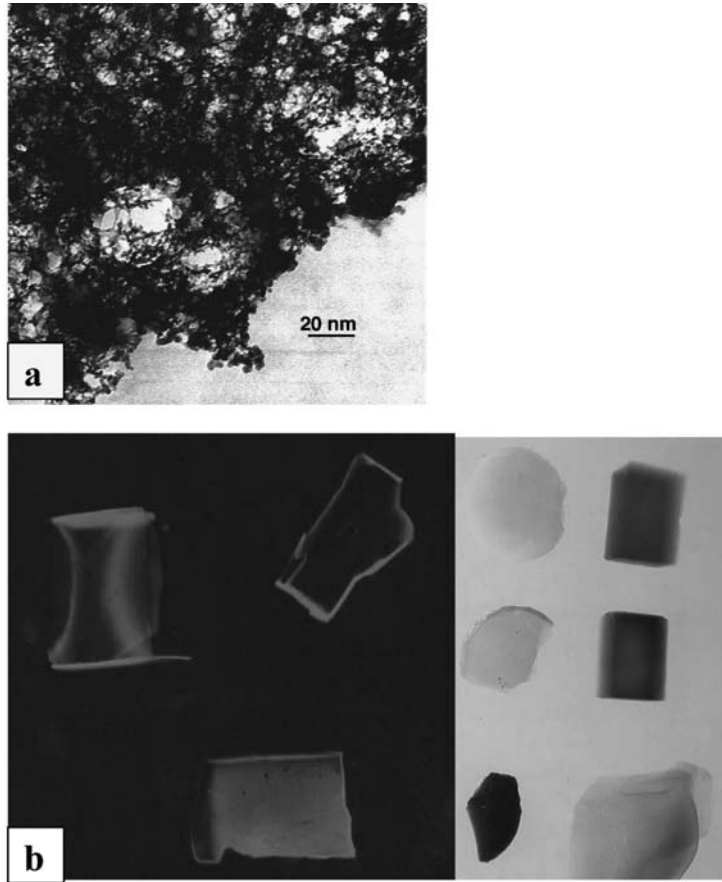
Fig. 1.4 (a) Microstructure of aerogel-encapsulated phase nanocomposite. (b) Left image of three pieces of nanocomposites shows silica aerogel samples that have been coated with silicon nanoparticles by chemical vapor methods. The composites emit red light when excited with ultraviolet light. Right image of six pieces of nanocomposites prepared by adding metal salts or other compounds to a sol before gelation; they show different colors depending on the metal species present. The deep blue aerogel contains nickel; the pale green, copper; the black, carbon and iron; the orange, iron oxide. (Source, the silica aerogel photo gallery [231] used with permission)

ticles within the aerogel matrix. Such composites can have many applications. An example is their use as catalysts for gas-phase reactions or for catalyzed growth of nanostructures.

Vapor phase infiltration through the open pore network of aerogels provides another route [25] to creating various forms of aerogel-based nanocomposites; almost any compound can be deposited uniformly throughout an aerogel. In fact, adsorbed materials in silica aerogels can be modified into solid phases by thermal or chemical decomposition. The same is true for materials that have a porous interior structure, such

as zeolites. The nanosize pores within these porous hosts can be utilized for depositing a second phase by chemical or vapor phase infiltration and thermal decomposition. Recently, single-walled carbon nanotubes have been deposited within pores of zeolites to create nanocomposite materials that have unique properties, such as superconductivity [26].

Some examples of nanocomposites (Figure 1.4) that have been created out of silica-based aerogel matrices are the following:

Silica aerogel/carbon composites [27]: These can be made by the decomposition of hydrocarbon gases at high temperatures. The fine structure of aerogels allows the decomposition to take place at a low temperatures (200–450 °C). Carbon loadings of 1 %–800 % have been observed. The carbon deposition is uniform throughout the substrate at lower loadings, but at higher loadings, the carbon begins to localize at the exterior surface of the composite. These nanocomposites have interesting properties, such as electrical conductivity (above certain loadings) and higher mechanical strength relative to the aerogel.

Silica aerogel/silicon composites [28]: Thermal decomposition of various organosilanes on a silica aerogel forms deposits of elemental silicon. In this case, rapid decomposition of the silane precursor leads to deposits localized near the exterior surface of the aerogel substrate. The nanocomposite, with 20–30-nm diameter silicon particles, exhibits strong visible photoluminescence at 600 nm.

Silica aerogel/transition-metal composites [29]: Organo/transition-metal complexes can be used to deposit metal compounds uniformly through the aerogel volumes. The compounds can be thermally decomposed to their base metals. These intermediate composites, due to the disperse nature of the metallic phase and hence their high reactivity, can be converted to metal oxides, sulfides, or halides. The loading of the metallic phase can be changed by repeated deposition steps. The nanocomposites contain crystals of the desired metal species with sizes in the range of 5–100 nm in diameter.

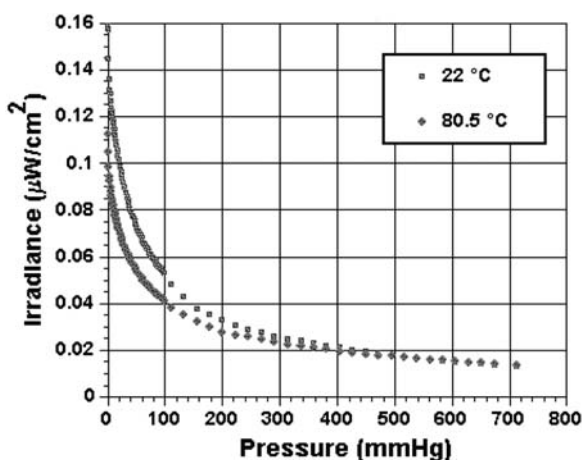**Fig. 1.5** Photoluminescence intensity (irradiance) vs. oxygen pressure (concentration gives a similar plot) at two temperatures measured with a prototype sensor made of silica aerogels. The photoluminescence intensity is indirectly proportional to the amount of gaseous oxygen within the aerogel. The quenching of photoluminescence by oxygen is observed in many luminescent materials. Source [232] used with permission)

The chemical structure of the silica (or other oxide) backbone of an aerogel can also be easily modified. For example, silica aerogel surfaces can be partially reduced by hydrogen. The resulting composite consists of thin interior surface layers of oxygen-deficient silica (SiO_x). This material exhibits strong visible photoluminescence at 490–500 nm when excited by ultraviolet (330 nm) light. The chemical process used to change the surface characteristics of the aerogel does not alter the physical shape or optical transparency of the original structure. This composite is the foundation for the aerogel optical oxygen sensor [30] (Figure 1.5), which is based on the fact that the intensity of photoluminescence is indirectly related to the oxygen concentration in the nanocomposite.

1.2.3
Nanocomposites by Thermal Spray Synthesis

Thermal spray processing is a commercially relevant, proven technique for processing nanostructured coatings [31]. Thermal spray techniques are effective because agglomerated nanocrystalline powders are melted, accelerated against a substrate, and quenched very rapidly in a single step. This rapid melting and solidification promotes the retention of a nanocrystalline phase and even amorphous structure. Retention of the nanocrystalline structure leads to enhanced wear behavior, greater hardness, and sometimes a reduced coefficient of friction compared to conventional coatings.

Figure 1.6 shows a generalized thermal spray process [32]. To form the starting powders, conventional powders can be cryomilled to achieve a nanocrystalline structure [33–35]. Under the right conditions, for example, Fe alloyed with Al, precipitates form, and these precipitates stabilize the nanoscale grain structure to 75 % of the melting temperature of the pure metal. Pure metals (except for aluminum) require some alloying before the nanocrystalline structure is stable at elevated temperatures [36]. For WC/Co and Cr_3Cr_2/NiCr, the hard particles are broken into nanometer-size grains, and they are embedded in the binder [37, 38]. Other systems have also been milled for thermal spraying, such as steel [39] and NiCr/Cr_3C_2. In all cases, there appears to be some nitrogen or oxygen contamination.

The nanoscale powders, prepared by various techniques, must be agglomerated so that grains on the order of 50 nm can be introduced into the thermal spray gun. Unlike sintering of ceramics, this agglomeration does not prevent full densification. A reasonably narrow particle size distribution ensures uniform heating. Nanocrystalline feedstock is generally injected internally (inside the torch), but powders can be injected externally. The type of flame or jet produced depends on the thermal spray technique, and within each technique, gas heating and gas flow parameters can control the velocity and temperature profile. The temperature and velocity profile, combined with the spray distance (the distance from the end of the nozzle to the substrate), control the temperature that the powders reach. Successive impact of particles in a molten or viscous state on the substrate or on previously deposited layers of material forms a coating.

The ability to maintain the nanocrystalline structure during processing and upon consolidation is critical to improving its properties because it is the nanoscale micro-
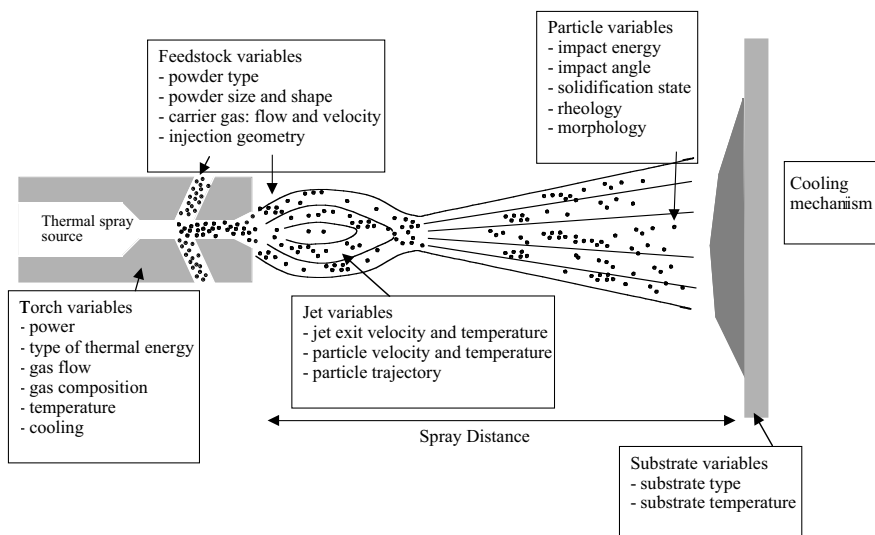
Fig. 1.6 Schematic for a generalized thermal spray process, showing the different variables used. The qualities of the coatings (bonding to the substrate, microstructure of the coating, hardness, wear resistance, etc.) are affected by a multidimensional parameter space

structure that leads to the unique properties. Several parameters are critical: (a) The thermal stability of the agglomerated powders: nanocrystalline materials can experience grain growth at temperatures well below the temperatures observed for conventional materials. The high surface area drives this growth. (b) The degree of melting that occurs in flight: this can be controlled by the spray distance, the temperature of the jet, and the velocity of the jet, and optimal parameters are determined primarily by experiment. (c) The cooling rate: a high cooling rate leads to high nucleation and slow grain growth, which promotes the formation of nanocrystalline grains. The systems that tend to maintain their nanocrystalline structure even at elevated temperature are apt to have impurities or a second phase that stabilize the grain structure [40]. For example, cryomilling often results in nanoscale particles (oxides, nitrides, or oxynitrides) [41] that fix the grain boundaries. In addition, significant impurities or excess solute atoms at the grain boundaries also limit grain growth [42, 43].

Plasma spraying and high velocity oxy fuel (HVOF) processes are the most widely used thermal spray methods for producing nanocrystalline and nanocomposite coatings. In plasma spraying, an electric arc is used to ionize an inert gas to produce a highly energetic thermal plasma jet with gas temperatures and velocities of approximately 11 000 K and 2000 ms^{-1}. Vacuum plasma spraying and low-pressure plasma spraying have been used to effectively process WC/Co nanocomposite coatings. Use of HVOF involves an internal combustion chamber in which fuel (hydrogen, propylene, acetylene, propane) is burned in the presence of oxygen or air (HVAF). This results in a hypersonic gas velocity. The particle velocities are higher than the 800 ms^{-1} achieved with plasma spray, and the thermal energy is lower (it may reach 3000 K), which reduces superheating and particle vaporization. The high speed and