

Organometallic route to nanocomposite synthesis

D CHAKRAVORTY

Advanced Centre for Materials Science, Indian Institute of Technology,
Kanpur 208 016, India

Present Address: Indian Association for the Cultivation of Science,
Jadavpur, Calcutta 700 032, India

Abstract. The nature and scope of different varieties of nanocomposite materials are described. The practical and basic aspects of the physical properties of nanocomposites are discussed. The principles underlying the preparation of diphasic materials involving either ceramic-metal or glass-metal combinations are delineated. The sol-gel technique involving suitable organometallic compounds has been shown to be a versatile method for making these materials. A brief survey is given about the different materials made to date following the organometallic route.

Keywords. Nanocomposite; organometallic compound; sol-gel; ceramic-metal composites; glass-metal composites; diphasic xerogel.

1. Introduction

Nanocomposites are materials containing one or more phases having dimensions of the order of a few nanometers dispersed in a suitable matrix (Roy & Roy 1984). Strictly speaking, the above definition should include solids containing defect clusters, e.g., the Willis (1964) clusters in UO_{2+x} and the Koch-Cohen (1969) clusters in $\text{Fe}_{1-\delta}\text{O}$ consisting of particular arrangements of vacancies and interstitials spread over several unit cells of the lattices concerned but coherently meshed in the host matrix. Solids exhibiting ordered or disordered intergrowth of two phases of similar structure but different compositions (Rao 1986, p. 10) could also fall under the same category. However, in the present discussion we restrict ourselves to systems which are diphasic (or multiphasic) in the phase rule sense.

There are a wide variety of nanocomposites which have been commercially exploited. Cermets consisting of fine metal grains dispersed in an oxide have been used as resistors in electronic circuits (Abeles *et al* 1975). Photosensitive, photochromic (Armistead & Stookey 1965), thermally darkenable photochromic (Seward 1975) and polychromatic glasses (Stookey *et al* 1978) depend for their respective properties on a microstructure consisting of nano-scale distribution of metal or halide particles within a glass matrix. The use of cobalt alumina cermets in solar photothermal conversion has been reported (Andersson *et al* 1980). Nano-size metal grains dispersed on a suitable substrate comprise an important group of catalysts for the chemical industry (Sinfelt 1977).

Glass-metal nanocomposites exhibit semiconduction due to electrons tunnelling from one metal grain to the next (Chakravorty *et al* 1977). In certain situations such composites have shown memory switching (Chakravorty & Murthy 1975). In some of the composites subjected to an ion-exchange treatment an enhanced ionic conductivity has been observed (Mozhi & Chakravorty 1982; Shrivastava & Chakravorty 1987). The latter phenomenon appears to have a correlation with the morphology of the glasses concerned at the nanolevel.

The physics of ultrafine particles has emerged as a rapidly growing field of research in recent years (Marlow 1982, p. 2). Most of the studies to date have been related to small metallic particles. Quantum-size effects have been investigated by measuring the specific heats of indium (Novotny & Meincke 1973) and palladium (Comsa *et al* 1977) nanoparticles. Analyses of electrical resistivity data for small particles of aluminium and silver show phonon softening (Ohshima *et al* 1977) as compared to that of the bulk material. Gorkov & Eliashberg (1965) theoretically predicted an anomalous enhancement of the static polarizability of fine metallic particles. Attempts at experimental verification of this phenomenon have, however, not proved successful so far (Meier & Wyder 1972; Dupree & Smithard 1972; Strassler & Rice 1972). Superconducting order as a function of particle size has been investigated theoretically (Schmidt 1967) and results predict a smooth temperature variation near the transition point. Such "rounded" phase transition in the so-called zero-dimensional superconductors has been studied by a variety of experimental techniques. Some of these are measurements of magnetic susceptibility on small aluminium particles (Buhrman & Halperin 1973), specific heat of granular aluminium films (Worthington *et al* 1978), ultrasonic attenuation in aluminium films (Tachiki *et al* 1975; Robinson *et al* 1974), nuclear magnetic resonance on fine aluminium and on tin particles (Kobayashi *et al* 1974). Thin films comprising small superconducting metallic grains have been reported to show a higher transition temperature as compared to bulk samples (Novotny & Meincke 1973). This phenomenon has been explained on the basis of surface phonon softening due to a high surface-to-volume ratio in these materials.

Apart from the effects of small size on the conventional properties of materials as explored by some of the investigations delineated above, studies on the electronic structure of ultra-fine metallic particles are expected to throw light on the understanding of the metallic and nonmetallic states of matter (Edwards 1986, p. 265). An interesting problem of fundamental importance in this regard is a possible metal-insulator transition at a critical diameter of the metallic particle (Wood & Ashcroft 1982).

It should be apparent from the above discussion that in order to investigate the effect of small size on the various physical properties of different materials one has to essentially prepare a nanocomposite comprising a distribution of small particles of the species in an inert matrix. Some of the conventional methods of preparing such composites have been discussed earlier (Chakravorty 1982). The sol-gel method has recently emerged as a versatile technique for preparing a wide variety of materials (Sen & Chakravorty 1986, p. 159). One of the most attractive features is that the processing can be carried out at fairly low temperatures. Glass-metal nanocomposites have recently been made by exploiting this method. The purpose of the present paper is to briefly review the present status of this technique.

2. Diphasic xerogels

Principles involved in the synthesis of di- or polyphasic xerogels with special reference to ceramic-metal composite systems have been discussed by Roy & Roy (1984). Two preparation routes have been proposed. In the first, a suitable solution containing all the components to be present in the ultimate product is prepared thereby forming a sol. The latter is then gelled, the process comprising the usual hydrolysis and polycondensation reactions (Yoldas 1982). After the desiccation step a xerogel is formed. Depending on the heat treatment given to the xerogel the product may lead to either a single-phase or a poly-phase material. In the second scheme the starting point is the preparation of a mixture of a sol comprising the oxide component and a solution containing the metallic salt, the latter acting as the metal phase precursor. After gelling this mixture it is dried to obtain the xerogel. This consists, in most of the cases studied by these workers, of two noncrystalline oxide phases, viz. the single component oxide and the heavy metal oxide phase, respectively. The two-phase solid prepared by either of the two processes described as above is then subjected to reduction treatment in a nitrogen and hydrogen gas mixture (95% N_2 , 5% H_2) at temperatures ranging from 200° to 700°C. Some of the starting materials used in the preparation of the different ceramic-metal composites are aluminium-isopropoxide, zirconyl chloride and silicon-tetraethoxide for the matrix phases and metallic salts like copper nitrate, stannous chloride and nickel nitrate for the metal phase. The presence of metallic islands of different types having diameters ranging from 5 to 50 nm has been verified by detailed electron microscopic investigation. In table 1 some of the preparational features have been summarised.

3. Glass-metal composites

Gels prepared from metal alkoxide solutions are porous and have large surface areas (Brinker & Scherer 1985). They should therefore be ideal materials for use as catalyst carriers. In fact, it was observed by Karatani & Minakuchi (1983) that glucose oxidase on silica gel made by the hydrolysis-polycondensation reaction of tetraethyl ethoxysilane exhibited a much higher enzymatic activity than that immobilized on conventional porous glasses. This high activity has been ascribed to the high density of silanol groups on the alkoxy-derived gel. This principle has been extended to the preparation of the catalyst-carrier composite, viz., small metal particles in a silica glass. Ueno *et al* (1983) prepared a catalyst system of Ni/SiO₂ by hydrolysing a mixed solution of Si(OC₂H₅)₄ and ethylene glycol solution of nickel hydroxide followed by drying, calcining and reduction treatment at 450°C. The metal particles were found to be highly dispersed, their sizes varying from 3 to 12 nm.

A variety of glass-metal nanocomposites have been investigated in the author's laboratory (Chakravorty 1984). Organometallic compounds have been used to prepare some composites of this type. Two approaches have been followed. In the first, a fairly low melting glass (essentially based on B₂O₃ in our case) has been prepared with a suitable organometallic compound forming one constituent of the raw materials used during the melting operation. The product after quenching has a structure consisting of fine metal granules with diameters ranging from 5–50 nm

Table 1. Summary of nanocomposites prepared by organometallic routes.

System	Method	Microstructural features	Properties measured	Reference
1. <i>Ceramic-metal composites</i>	Sol + solution ↓ Gel ↓ Xerogel ↓ Reduction treatment ↓ Ceramic metal composite	Noncrystalline (or microcrystalline) ceramic matrix with small metallic islands of size varying between 5–50 nm	Photo-sensitivity	Roy & Roy (1984) Hoffman <i>et al</i> (1984)
Al ₂ O ₃ ; copper Platinum, Nickel Zirconia: Copper Nickel Silica: copper, Tin				
2. <i>Glass-metal composites</i>	Hydrolysis of a mixed solution of Si(OC ₂ H ₅) ₄ and ethylene glycol solution of nickel hydroxide ↓ Gel ↓ Reduction Glass-metal composite	Nickel particles of size between 3 and 12 nm	Catalytic activity	Ueno <i>et al</i> (1983)
(a) Ni/SiO ₂				
(b) Ni/50 BaO, 50B ₂ O ₃ (wt%) Nickel content: varying between 0.1 and 0.3 wt%	Melting of mixture of oxide components and Ni(C ₉ H ₆ ON) ₂ ·2H ₂ O	Nickel particles of size between 5 and 8 nm	Optical absorption Magnetic behaviour	Datta & Chakravorty (1983) Datta <i>et al</i> (1984)
(c) Ni/SiO ₂ Nickel content: 0.8 wt%	Sol of Si(OC ₂ H ₅) ₄ and Ni(C ₉ H ₆ ON) ₂ ·2H ₂ O ↓ Gel ↓ Xerogel	Particle size between 5 and 30 nm	Magnetic behaviour	Datta <i>et al</i> (1986)
(d) Co/50BaO 50B ₂ O ₃ (wt%) Cobalt content 0.4 wt% (approximately)	Melting of oxide components with [Co(C ₅ H ₅ N) ₄](SCN) ₂	Particle size between 5 and 35 nm	—	S S Mitra & D Chakravorty (1986, unpublished)
e) Pd/50BaO 50B ₂ O ₃ (wt%) Palladium content: Varying between 0.1 and 0.3 wt% (approximately)	Melting of oxide components with [Pd(C ₅ H ₅ N) ₄](SCN) ₂	Particle size between 3 and 9 nm	—	S S Mitra & D Chakravorty (1986, unpublished)

dispersed in the glass matrix. The choice of the organometallic species obviates the need for the reduction step as followed by previous workers. It is believed that

favourable oxygen fugacities are attained locally within the melt as a result of the breaking up of the compound which releases carbon, hydrogen and nitrogen atoms. The composites prepared so far consist of nickel, cobalt and palladium respectively in a barium borate glass. Nickel has been introduced in the form of oxinate $\text{Ni}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 2\text{H}_2\text{O}$ (Datta & Chakravorty 1983), cobalt and palladium as complexes formed between pyridine and the corresponding thiocyanates $[\text{Co}(\text{C}_5\text{H}_5\text{N})_4](\text{SCN})_2$ and $[\text{Pd}(\text{C}_5\text{H}_5\text{N})_4](\text{SCN})_2$, respectively. The amounts of metal content in the glasses range between 0.1 and 0.4 wt%.

In the second technique, a sol is first prepared containing both the glass and the metal precursors, viz. silicon tetraethoxide and nickel oxinate, in ethyl alcohol. The sol is then allowed to gel and subsequently dried, cooled and then heat-treated to a temperature of around 750°C for 2 h (Datta *et al* 1986). The resultant product has a microstructure consisting of fine metallic nickel granules having diameters in the range 5 to 30 nm dispersed in the silica glass matrix. Table 1 gives a summary of the salient features of the preparational and characterization aspects of the above materials.

So far the physical properties investigated comprise only the optical absorption (Datta & Chakravorty 1983), magnetic susceptibility and EPR (Datta *et al* 1984, 1986). The optical absorption has been explained satisfactorily on the basis of the usual effective medium theories (Granqvist & Hunderi 1977). Low temperature magnetic susceptibility of nickel nanogranules in borate glass shows a broad range of transition temperatures between 77 K and 300 K. A similar trend has also been shown by the EPR data. The results indicate a superparamagnetic behaviour. It is expected, however, that with narrow distribution of particle sizes of the metallic species effected by controlling the process parameters, it will be possible to undertake investigations on some of the fundamental aspects of fine particle physics.

4. Concluding remarks

Organometallic compounds have been used to make nanocomposite materials of the ceramic-metal and glass-metal varieties respectively. The processing parameters have been investigated by several workers. It now seems possible to combine a wide variety of metallic species with different oxide systems in a composite structure by suitable choice of starting materials. A more recent innovation has been to exploit the compositional heterogeneity on a "nano" scale to make densified products in several oxide systems (Komarneni *et al* 1986). It is expected that the sol-gel technique of materials processing of the type discussed in this article will lead to preparation of materials exhibiting novel physical properties.

References

- Abeles B, Sheng P, Coutts M D, Arie Y 1975 *Adv. Phys.* 24: 407-461
- Andersson A, Hunderi O, Granqvist C G 1980 *J. Appl. Phys.* 51: 754-764
- Armistead W H, Stookey S D 1965 US Pat. no. 3108860
- Brinker C J, Scherer G W 1985 *J. Non-Cryst. Solids* 70: 301-322
- Buhrman R A, Halperin W P 1973 *Phys. Rev. Lett.* 30: 692-695

- Chakravorty D 1982 *Curr. Sci.* 51: 671-676
- Chakravorty D 1984 *Bull. Mater. Sci.* 6: 193-200
- Chakravorty D, Bandyopadhyay A K, Nagesh V K 1977 *J. Phys. D: Appl. Phys.* 10: 2077-2087
- Chakravorty D, Murthy C S 1975 *J. Phys. D: Appl. Phys.* 8: L162-L165
- Comsa G H, Heitkamp D, Rade H S 1977 *Solid State Commun.* 24: 547-550
- Datta S, Bahadur D, Chakravorty D 1984 *J. Phys. D: Appl. Phys.* 17: 163-169
- Datta S, Chakravorty D 1983 *J. Mater. Sci. Lett.* 2: 329-331
- Datta S, Mitra S S, Chakravorty D, Ram S, Bahadur D 1986 *J. Mater. Sci. Lett.* 5: 89-90
- Dupree R, Smithard M A 1972 *J. Phys. C: Solid State Phys.* 5: 408-414
- Edwards P P 1986 in *Advances in solid state chemistry* (ed.) C N R Rao (New Delhi: Indian National Science Academy)
- Gorkov L P, Eliashberg G M 1965 *Zh. Eksp. Teor. Fiz.* 48:1407 [Engl. Transl.: *Sov. Phys. JETP* 1965 21: 940-947]
- Granqvist C G, Hunderi O 1977 *Phys. Rev.* B16: 3513-3534
- Hoffman D, Komarneni S, Roy R 1984 *J. Mater. Sci. Lett.* 3: 439-442
- Karatani H, Minakuchi H 1983 *J. Chem. Soc. Jpn.* (11): 1577 (in Japanese)
- Kobayashi S, Takahashi T, Sasaki W 1974 *J. Phys. Soc. Jpn.* 36: 714-719
- Koch F B, Cohen J B 1969 *Acta Cryst.* B25: 275-287
- Komarneni S, Suwa Y, Roy R 1986 *J. Am. Ceram. Soc.* 69[7]: C155-C156
- Marlow W H (ed.) 1982 *Aerosol microphysics II* (Berlin, Heidelberg, New York: Springer Verlag)
- Meier F, Wyder P 1972 *Phys. Lett.* A39: 51-52
- Mozhi T A, Chakravorty D 1982 *J. Mater. Sci. Lett.* 1: 426-428
- Novotny V, Meincke P P M 1973 *Phys. Rev.* B8: 4168-4199
- Ohshima K, Fujita T, Kuroishi T 1977 *J. Phys. (Paris)* C2-38: 163-165
- Rao C N R (ed.) 1986 *Advances in solid state chemistry* (New Delhi: Indian National Science Academy)
- Robinson D A, Maki K, Levy M 1974 *Phys. Rev. Lett.* 32: 709-712
- Roy R A, Roy R 1984 *Mater. Res. Bull.* 19: 169-177
- Schmidt V V 1967 in *Proc. 11th Int. Conf. on Low Temperature Physics* (ed.) M P Malkow (Moscow: Moscow Publishing House)
- Sen A, Chakravorty D 1986 in *Advances in solid state chemistry* (ed.) C N R Rao (New Delhi: Indian National Science Academy)
- Seward T P III 1975 *J. Appl. Phys.* 46: 689-694
- Shrivastava A, Chakravorty D 1987 *J. Phys. D: Appl. Phys.* 20: 380-385
- Sinfelt J H 1977 *Science* 195: 641-646
- Stookey S D, Beall G H, Pierson J E 1978 *J. Appl. Phys.* 49: 5114-5123
- Strassler S, Rice M J 1972 *Phys. Rev.* B6: 2575-2577
- Tachiki M, Salvo H, Robinson D A, Levy M 1975 *Solid State Commun.* 17: 653-656
- Ueno A, Suzuki H, Kotera Y 1983 *J. Chem. Soc., Faraday Trans.* 79: 127-136
- Willis B T M 1964 *Proc. Br. Ceram. Soc.* 1: 9
- Wood D M, Ashcroft N W 1982 *Phys. Rev.* B25: 6255-6276
- Worthington T, Lindenfeld P, Deutscher G 1978 *Phys. Rev. Lett.* 41: 316-319
- Yoldas B E 1982 *J. Non-Cryst. Solids* 51: 105-121