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Electrical properties of sol–gel-derived glass–metal nanocomposites

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Abstract. Composites of silica glass and metal nanoparticles of copper or nickel have been synthesized by the hot compaction of sol–gel-derived glass–metal powders. The metal particle sizes range from 5.1 to 7.2 nm. The electrical resistivity of the composites is characterized by semiconductor-like behaviour in the temperature range 235–340 K. This is believed to arise owing to electron hopping between localized states within the band gap of amorphous silica formed by the dispersed metal atoms. A low activation energy of the order of a few millielectronvolts in the specimens containing copper in the temperature range 140–235 K may occur because of a quantum size effect, the metal particles forming continuous chains with diameters of the order of 3 nm.

1. Introduction

Nanophase materials have been receiving considerable attention lately because of some of the unusual physical properties which they exhibit (Horvath *et al* 1987, Siegel *et al* 1988, Nieman *et al* 1990). Different physical and chemical methods have been used by different investigators for making nanoclusters of metals or inorganic compounds (Chakravorty and Giri 1992). We have used techniques in which nanosized metal particles are grown within an inert medium such as glass or glass–ceramic. The electrical properties of these small particles have been measured by bringing the metal phase into a percolation configuration (Roy and Chakravorty 1990, Chatterjee and Chakravorty 1992a) within the glassy or glass–ceramic medium. Recently, we have reported a technique for preparing bulk composites consisting of nanosized metal particles in a sol–gel-derived glass matrix (Roy *et al* 1993). The preliminary results refer to the delineation of metallic resistivity as a function of temperature. We have now prepared samples which also exhibit semiconducting behaviour. The metallic species chosen in this study are copper or nickel in a silica glass matrix. The results are reported in this paper.

2. Experimental details

The starting materials used for sample preparation are an inorganic salt of the metal concerned and $\text{Si}(\text{OC}_2\text{H}_5)_4$. The salts used are $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ for copper and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ for nickel. A solution of the metallic salt and silicon tetraethoxide of weighed amount is prepared in a measured volume of ethyl alcohol with a few drops of 30 N nitric acid. The amounts of the precursors are taken in such a way that the calculated value of the volume fraction of metal phase is 0.2 in the final nanocomposite, assuming that all the

metal ions have been reduced. The mixture is stirred in a magnetic stirrer for 1 h to obtain a clear sol. This is then poured into a plastic flat-bottomed container and gelled in the ordinary atmosphere for 3–4 d. The gel pieces are ground in a mortar and then subjected to a reduction treatment in hydrogen at temperatures ranging from 773 to 873 K for a maximum period of 35 min. The hydrogen-reduced particles are again crushed in a mortar and the powder thus obtained is placed in a graphite mould of 1.5 cm diameter. The mould assembly is mounted in a sintering press type DSP 25ATS (manufactured by M/s Dr Fritsch Sondermaschinen, Germany). The powders are pressed in an ambient pressure of 0.26 bar at temperatures varying from 773 to 873 K for 1 min, applying a pressure of 2.4 MPa. The specimens thus prepared have an approximate thickness of 1 mm.

The microstructure of the nanocomposites has been studied using a JEM 200 CX transmission electron microscope. The sample preparation for electron microscopy has been described earlier (Chatterjee and Chakravorty 1992b).

For electrical measurements, silver paint (supplied by Acheson Colloiden BV Netherlands) is applied on the two faces of the specimens. The electrical resistances of the different specimens are measured over the temperature range 80–340 K using a Keithley 617 electrometer.

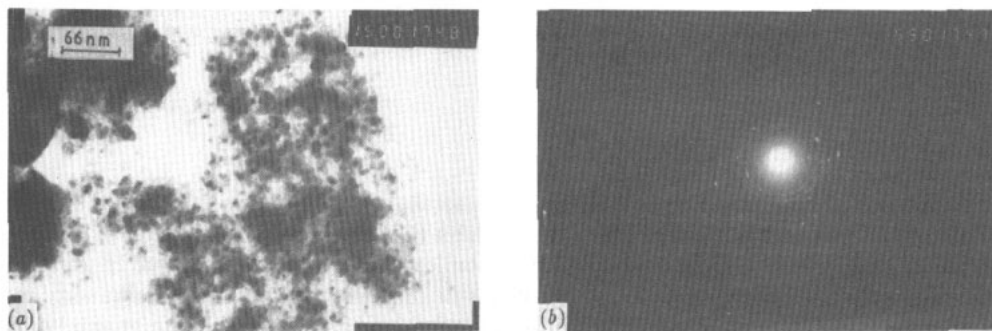


Figure 1. (a) Transmission electron micrograph for sample Cu-2. (b) Selected-area electron diffraction pattern of (a).

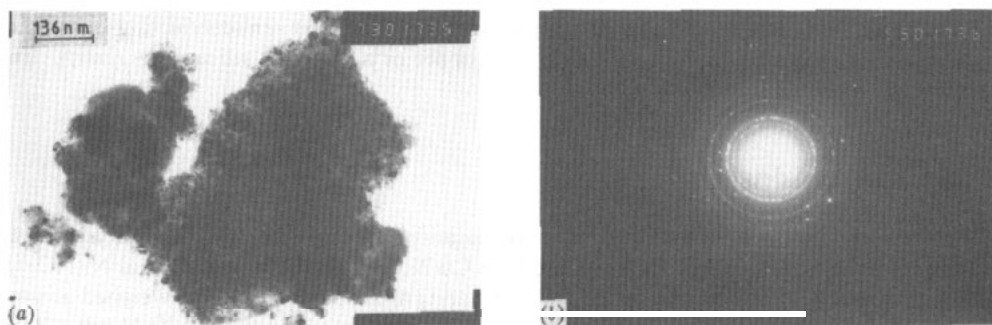


Figure 2. (a) Transmission electron micrograph for sample Ni-2. (b) Selected-area electron diffraction pattern of (a).

3. Results and discussion

In table 1 is summarized the heat treatment schedules used for the preparation of different nanocomposites. Figure 1(a) is the transmission electron micrograph for the glass-metal composite containing copper which has been reduced in hydrogen at 773 K for 20 min and subsequently hot pressured at 773 K for 1 min with a pressure of 2.4 MPa. Figure 1(b) shows the electron diffraction pattern of figure 1(a). Figure 2(a) gives the transmission electron micrograph for the nanocomposite containing nickel which has been reduced at 823 K for 35 min and subsequently consolidated at 823 K for 1 min using a pressure of 2.4 MPa. Figure 2(b) is the electron diffraction pattern of figure 2(a). The interplanar spacings d_{hkl} calculated from the diameter of these rings are compared with standard ASTM values for metallic copper and nickel. The data are shown in table 2. The observed values are in satisfactory agreement with the standard values, thus confirming the presence of the corresponding metal phase within the composite concerned. It is to be noted, however, that the values of 0.1497 nm and 0.1452 nm for Cu-2 and Ni-2 do not match any of the standard interplanar spacings of these metals. These appear to indicate the presence of CuO ($d_{hkl} = 0.1510$ nm) and NiO ($d_{hkl} = 0.1476$ nm) in specimens Cu-2 and Ni-2, respectively. The formation of oxide layers on the small metal particles might have occurred in these samples. Similar results have been obtained for all the specimens investigated. Figure 3 is a typical histogram showing the particle size distribution in the case of specimen Cu-2. The points in this figure refer to the experimental data and the solid line is the theoretical curve obtained by fitting these data to the log-normal distribution function which can be written as

$$\Delta n = \frac{1}{\sqrt{2\pi} \ln \sigma} \exp \left\{ -\frac{1}{2} \left[\ln \left(\frac{x}{\bar{x}} \right) / \ln \sigma \right]^2 \right\} \Delta(\ln x) \tag{1}$$

where Δn is the fractional number of particles per logarithmic diameter interval $\Delta(\ln x)$, \bar{x} the median diameter and σ the geometric standard deviation. A summary of metal particle diameters and the geometric standard deviation for the different specimens is given in table 1. It is evident that the metal particle diameter can be increased by suitably increasing the reduction treatment. A nucleation-and-growth mechanism is believed to be responsible for the formation of the metallic nanoparticles at the surface of the gel-derived silica glass grains during the reduction treatment (Chatterjee and Chakravorty 1992b).

Table 1. Heat treatment schedule and metal particle diameters in different nanocomposites.

Specimen	Metal phase	Heat treatment schedule in H ₂	Hot-pressing conditions	Average particle diameter \bar{x} (nm)	Geometric standard deviation σ
Cu-1	Cu	773 K for 35 min	2.4 MPa; 773 K for 1 min	7.2	1.5
Cu-2	Cu	773 K for 20 min	2.4 MPa; 773 K for 1 min	5.5	1.5
Cu-3	Cu	773 K for 10 min	2.4 MPa; 773 K for 1 min	5.3	1.5
Ni-1	Ni	873 K for 35 min	2.4 MPa; 873 K for 1 min	6.9	1.4
Ni-2	Ni	823 K for 35 min	2.4 MPa; 823 K for 1 min	5.6	1.5
Ni-3	Ni	773 K for 35 min	2.4 MPa; 773 K for 1 min	5.1	1.5

Table 2. Comparison of d_{hkl} -values with standard ASTM data for specimens Cu-2 and Ni-2.

Specimen	d_{hkl} (nm)	
	Observed	Standard
		Cu
Cu-2	0.2088	0.2088
	0.1812	0.1808
	0.1497	
	0.1275	0.1278
	0.1075	0.1090
	0.0815	0.0808
Ni-2	0.2034	0.2034
	0.1726	0.1762
	0.1452	
	0.1227	0.1246
	0.0868	0.0881
	0.0769	0.0788

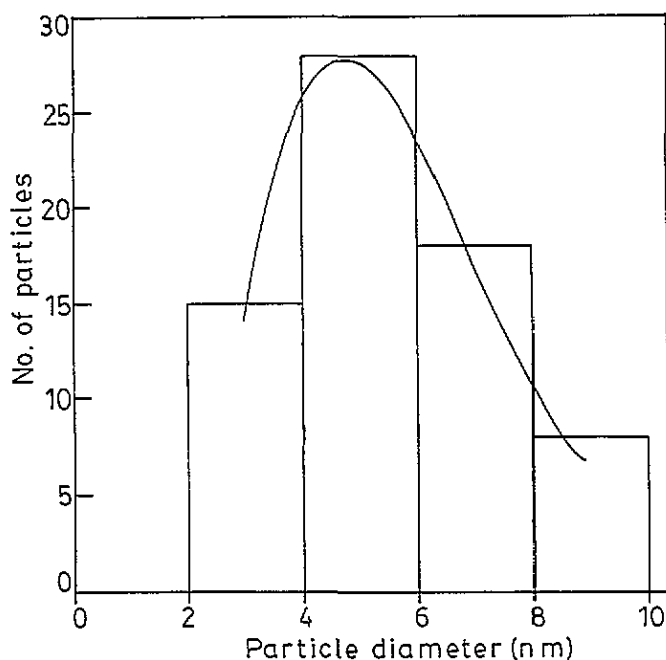


Figure 3. Particle size distribution in sample Cu-2.

Figures 4 and 5 show the variation in resistivity as a function of inverse temperature for different specimens containing copper and nickel nanoparticles, respectively. The reproducibility of the resistivity data has been checked by repeating the measurements at least twice on the same sample as well as on at least two samples prepared under identical conditions. The data are found to be reproducible to within 1%. Any possible influence of the electrical contacts on the measured value of resistances of different specimens has also

been investigated by carrying out measurements on samples whose thickness and area of cross-section have been changed, respectively. In table 3 a typical set of data is given for specimens Cu-1 and Cu-2. It is evident that the sample resistance scales inversely as its area of cross-section and scales directly as its thickness. The electrical resistivity data reported therefore correspond to the sample properties and are not influenced by the contacts or leaking currents. The copper-containing samples exhibit three different slopes in the curves concerned. There is a sharp increase in resistivity in the temperature range 340–235 K followed by a small change in resistivity down to about 140 K. For temperatures below about 140 K, specimens Cu-1 and Cu-3 exhibit a metallic resistivity as evidenced by the negative slopes of the curves concerned. The latter trend has, however, not been observed in the case of specimen Cu-2. In the case of composites containing nickel nanoparticles the resistivity change is characterized by semiconductor-like behaviour in the temperature range 140–340 K and metallic behaviour in the range 80–140 K. The scatter of the data obtained is considerable. Hence the exact values of the activation energies in different temperature ranges as computed by fitting straight lines to the curves concerned will not be meaningful. However, it would be interesting to estimate the orders of magnitude of these energies and then to speculate on the possible mechanisms of electrical transport.

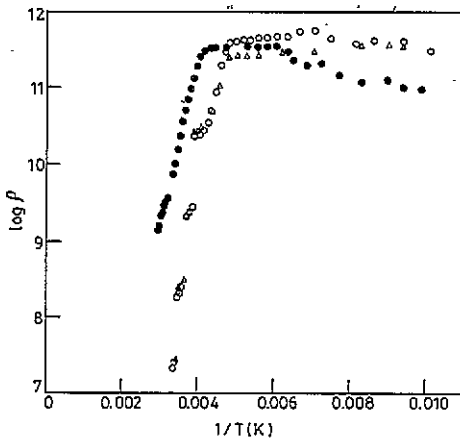


Figure 4. Resistivity variation as a function of inverse temperature for samples containing copper nanoparticles: O, Cu-1; Δ , Cu-2; \bullet , Cu-3.

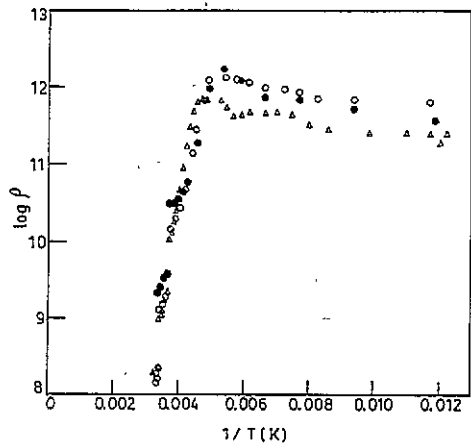


Figure 5. Resistivity variation as a function of inverse temperature for samples containing nickel nanoparticles: O, Ni-1; Δ , Ni-2; \bullet , Ni-3.

The slopes of the curves in the temperature range 235–340 K indicate an activation energy of the order of 0.40 eV. From the microstructure of the samples it appears likely that the electrical conduction in this temperature region is controlled by electron tunnelling (Neugebauer and Webb 1962) between the nanosized metal particles. The activation energies calculated from the equation of Tick and Fehlner (1972) using the metal particle diameter and inter-particle separation as obtained from the electron micrographs, however, are much smaller than those estimated from experimental data. We therefore believe that the electrical conduction is due to a hopping mechanism between the localized states which form within the band gap of amorphous silica because of the presence of distributed metal atoms in it (Moyo and Leaver 1980, Chatterjee and Chakravorty 1990). As the reduction treatment is enhanced, the average metal particle diameter increases. At the same time the number of dispersed metal atoms also increases. This would decrease the separation between the

Table 3. Typical scaling of sample resistances with physical dimensions.

Specimen	Area of cross section	Resistance		
	A (mm ²)	R (M Ω)	R_1/R_2	A_2/A_1
Cu-1	14	275	2.11	2.07
Cu-1	29	130		
Specimen	Thickness	Resistance		
	t (mm)	R (M Ω)	R_1/R_2	t_1/t_2
Cu-2	1.30	1.50	1.75	1.63
Cu-2	0.80	0.857		

localized states, which in turn should lower the activation energy for the hopping type of conduction. Such a trend in activation energy value is in fact shown by our data.

The low activation energy (of the order of a few millielectronvolts) as extracted in the temperature range 140–235 K for specimens Cu-1, Cu-2 and Cu-3 cannot be explained on the basis of electron tunnelling mechanism. A possible model is the existence of a few continuous chains formed by very small particles whose effect shows up only when the overall resistance level of the sample is high. For metal particles with small diameters the energy levels become discrete and the separation Δ between these levels can be expressed as (Kubo 1962, Wood and Ashcroft 1982)

$$\Delta \sim E_F/N \quad (2)$$

where E_F is the Fermi energy of the bulk metal concerned and N the total number of atoms within the particle. Taking $\Delta \simeq 5$ meV, $E_F = 7.05$ eV and the lattice parameter of copper $a = 0.361$ nm, we calculate a value for the diameter of about 3.1 nm. Chains of such metal particles may therefore behave like a semiconductor with a low activation energy.

In summary, we have synthesized a series of glass-metal composites containing copper or nickel nanoparticles using silica as the glass matrix. The composites exhibit semiconductor-like behaviour in the temperature range 235–340 K. This is believed to arise owing to hopping of electrons between localized states within the band gap of amorphous silica formed by dispersed metal atoms. A very low activation energy in the specimens containing copper in the temperature range 140–235 K is believed to be the result of a quantum size effect of very small metal particles forming a few continuous chains.

Acknowledgments

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