

## Preparation of glass–nickel microcomposites by *in situ* reduction via sol–gel route

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**Abstract.** Gel has been prepared with nickel chloride and glucose in the starting solution followed by heat treatment at higher temperature, where glucose decomposes to carbon and water vapour, which in turn react to form hydrogen *in situ* to reduce nickel chloride to metallic nickel. The presence and distribution of nickel granules in the microcomposite, has been established by transmission electron microscopy, selected area diffraction and electron paramagnetic resonance analysis.

**Keywords.** *In situ* reduction; glass nickel microcomposites; sol–gel.

### 1. Introduction

Glass metal microcomposites possess interesting optical (Chakravorty *et al* 1975; Granqvist and Hunderi 1977; Das *et al* 1983), electrical (Chakravorty *et al* 1977; Das *et al* 1978; Das and Chakravorty 1980) and magnetic properties (Dutta *et al* 1984) which are functions of shape, size, distribution and the amounts of metallic microgranules present. By conventional methods, only a limited number of metallic species in small amounts can be precipitated in glass (Chakravorty *et al* 1977; Das and Chakravorty 1980). The preparation of glass–metal micro-composites through sol–gel techniques is rather rare (Carturan *et al* 1982; Roy and Roy 1984). Hence the preparation of glass–nickel micro-composite through the sol–gel route by *in situ* reduction has been attempted. The results of this investigation are reported in this work.

### 2. Experimental

Table 1 gives the batch compositions which have been investigated. Required amounts of nickel chloride and glucose are weighed and dissolved completely in 6.5 ml distilled water. To this solution 10 ml of dehydrated ethyl alcohol is added and a homogeneous solution is prepared. 10 ml of ethyl alcohol are then added to 5 ml of TEOS to make a homogeneous solution. The first solution is then added dropwise to the latter with constant stirring. One or two drops of concentrated HCl is added for adjusting the pH of the solution in the range 1.8 to 2.2. The solution comprising TEOS, ethyl alcohol, water, nickel chloride and glucose is then heated over a heating mantle at about 60°C for 16 to 18 hours for the formation of a gel. Hydrated nickel chloride and glucose are present in the pores of the dried gel. The dried gel (sample 1) is introduced in a tubular furnace at a temperature of 950°C in a carbon monoxide

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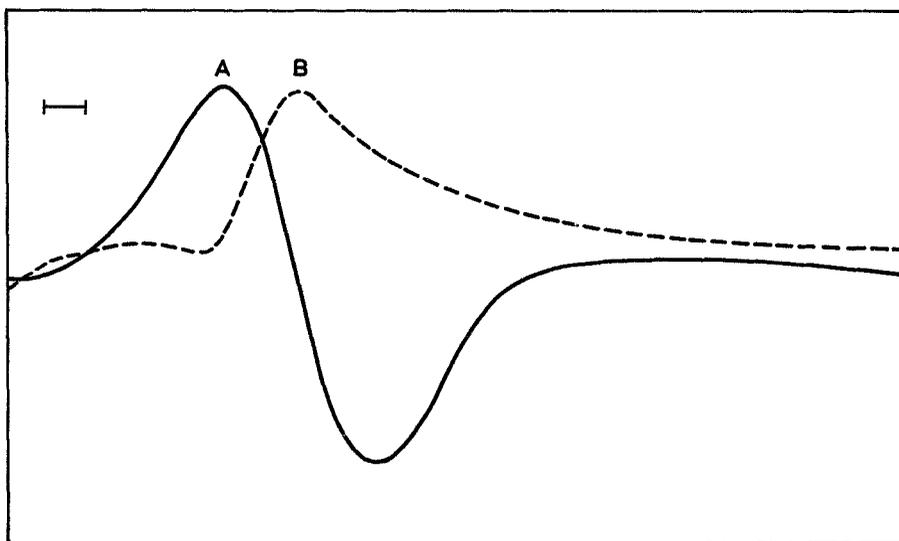
**Table 1.** Batch composition of glass-nickel microcomposites.

Sample	TEOS (ml)	Water (ml)	Dehydrated ethyl alcohol (ml)	Nickel chloride (g)	Glucose (g)
1	5.0	6.5	20.0	0.1520	0.0369
2	5.0	6.5	20.0	0.3040	0.0738

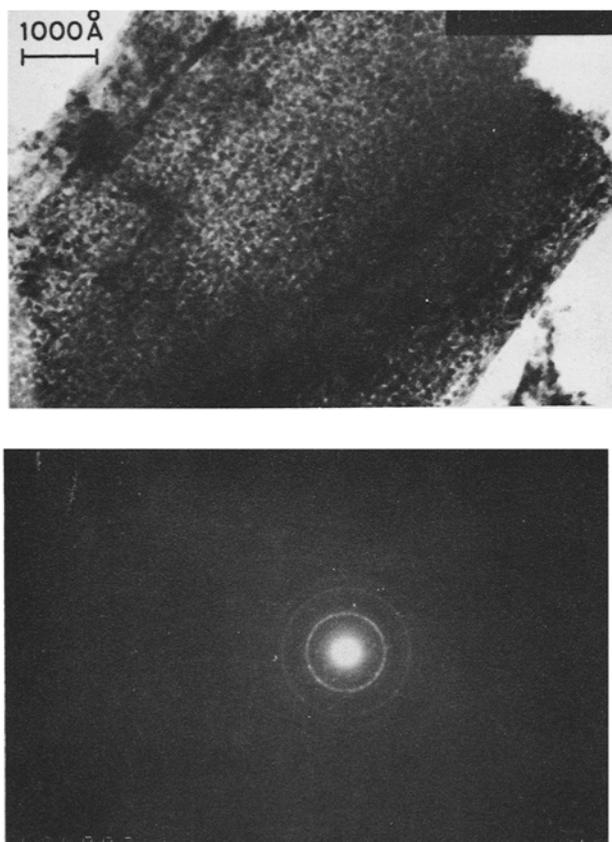
atmosphere for a period of one hour. The carbon monoxide atmosphere is obtained by using activated charcoal in the tubular furnace for the generation of an excessive reducing atmosphere to prevent the subsequent oxidation of Ni. The dried gel (sample 2) is inserted into the tubular furnace maintained at 950°C for a period of one hour in a nitrogen atmosphere.

### 3. Results and discussion

The electron paramagnetic resonance (EPR) spectra of 350 mesh heat-treated powdered samples were recorded with a Varian model E109 spectrometer at room temperature (298 K) using  $x$  band cavity and 100 kHz modulation frequency. The magnetic field is standardised with DPPH. Figure 1 shows the EPR spectra for samples 1 and 2. The field set and scan range for samples 1 and 2 are 3390 gauss, 2 kilogauss, and 3990 gauss and 4 kilogauss, respectively. The microstructure of two samples is studied by transmission electron microscopy (JEM-200  $\times$  JEOL). The typical microstructure and the corresponding selected area diffraction (SAD) pattern



**Figure 1.** EPR spectra, (A) for sample 1 reduced at 950°C for 1 hour in a CO atmosphere, and (B) for sample 2 reduced at 950°C for 1 hour in an N<sub>2</sub> atmosphere. Bar indicates 100 G and 200 G for A and B respectively.



**Figure 2.** (a) Electron micrograph of sample 1. (b) Selected area diffraction pattern of sample 1.

for sample 1 are shown in figures 2a and 2b respectively. From the EPR spectra, the computed  $g$  values for samples 1 and 2 are 2.224 and 2.20, respectively. These indicate the presence of metallic nickel (Che *et al* 1980). The radii of the diffraction rings have been measured from the photographic negative of figure 2b to compute the interplanar spacings,  $d_{hkl}$ . Table 2 contains the computed interplanar spacings  $d_{hkl}$  and the standard  $d_{hkl}$  values for nickel (Powder Diffraction File 1967). The computed  $d_{hkl}$  values match reasonably well with those of standard values and hence metallic nickel is present in the composite. The average size of nickel granules as computed from the micrograph (figure 2a) is 75 Å while that for sample 2 is 104 Å. The metallic nickel in the micro-composites has been estimated by using an atomic absorption spectrophotometer (Perkin–Elmer Model No. 2380). The Ni/SiO<sub>2</sub> ratios of samples 1 and 2 are 0.013 and 0.004, respectively.

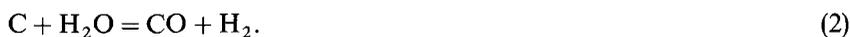
We propose the following mechanism of reduction. At high temperature glucose breaks up giving rise to activated carbon and water vapour at about 280°C.

The activated carbon reacts with water vapour obtained from the glucose and from the gel to form hydrogen by the following reactions,



**Table 2.** Comparison of  $d_{hkl}$  values (Å) as computed from SAD pattern of sample 1 with standard values for nickel.

Computed values	Standard values
1.540	—
1.253	1.246
1.050	1.062
0.898	0.881
0.773	0.788
0.560	—
0.516	—



The hydrogen so generated reduces nickel chloride which is present in the pores of the gel by the reaction,



Thus hydrogen is generated *in situ* to reduce the nickel chloride to form glass–nickel microcomposites through the sol–gel route.

### Acknowledgements

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