Preparation of alumina–silica–nickel nanocomposite by in situ reduction through sol–gel route

A. Bhattacharyya\textsuperscript{a,*}, P.C. Chakraborti\textsuperscript{b}, S. Mukherjee\textsuperscript{b}, M.K. Mitra\textsuperscript{a}, G.C. Das\textsuperscript{b}

\textsuperscript{a}School of Material Science and Technology, Jadavpur University, Calcutta 700 032, India
\textsuperscript{b}Department of Metallurgical Engineering, Jadavpur University, Calcutta 700 032, India

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Abstract

Ceramic based composites with dispersion of nano sized metal/metal carbide particles have generated wide technological interest for their improved mechanical properties — hardness, fracture strength as well as fracture toughness, superior electrical properties and magnetic properties. In the present investigation alumina–silica gels have been prepared along with nickel chloride and dextrose distributed in the nanometric pores of the gel. The gels are prepared with different molar proportions of alumina and silica containing 5 wt% of nickel chloride and 50 wt% excess dextrose. During heat treatment at a temperature of 900°C for half an hour in nitrogen atmosphere, nickel chloride is reduced to metallic nickel by in situ generated hydrogen in the silica–alumina matrix. X-ray analyses indicate that no nickel chloride reduction is possible upto 50 mol% silica in alumina–silica matrix. Beyond this range, higher the silica content, higher is the reduction of nickel chloride. The presence of metallic nickel has been substantiated further by SAD analysis. Particle size analysis based on X-ray diffraction as well as transmission electron micrograph shows the presence of nickel particles of size $\sim$20 nm distributed in the alumina–silica nanocomposite. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Alumina–silica–nickel nanocomposite; In situ reduction; Sol–gel route

1. Introduction

Nanocomposite materials have generated profound interest because of the new physics of nano particles and many potential applications based on improved electrical properties and superior mechanical properties like hardness, fracture strength, and fracture toughness [1]. Nanocomposite may be defined as the distribution of a second phase of nanometric dimension in a matrix — amorphous or crystalline. Large number of physical and chemical methods for the preparation of these materials have recently been reviewed by Banerjee and Chakraborty [2]. Out of the different chemical methods sol–gel is a very promising and versatile route for the preparation of nanocomposites, particularly glass–metal nanocomposites. These are usually made by reducing metallic salts in the pores of gel by passing hydrogen from outside [3]. In our laboratory, for over a decade, glass–transition metal nanocomposites have been successfully prepared by reducing transition metal salts in the pores of silica gel by in situ generation of hydrogen [4,5] and the kinetics of reduction has been extensively studied [6–8]. Recently the same reduction technique has been utilized to make SiO$_2$–WC nanocomposites [9]. Reduction of NiO in Al$_2$O$_3$ matrix followed by hot pressing leads to the fabrication of Al$_2$O$_3$–Ni nanocomposite with improved fracture strength, fracture toughness, and high temperature hardness [10]. Detailed information is available on the formation of Al$_2$O$_3$–SiO$_2$ gel [11,12]. In this paper we present the results of the preparation of Al$_2$O$_3$–SiO$_2$–Ni nanocomposites by in situ reduction through the sol–gel method.

2. Experimental

Clear sols corresponding to alumina and silica have been prepared separately and mixed in the molar ratio of 0, 1:0.5, 1:1, 1:2 and 1:4 under constant stirring. Silica sol contained nickel chloride and dextrose. The amount of nickel chloride present corresponds to 5 wt% nickel with respect to silica–alumina matrix. Dextrose has been added 50% in excess of the stoichiometric requirement for reduction of nickel chloride. Yoldas [13] method has been followed for the preparation of alumina sol while the preparation of silica sol containing nickel chloride and dextrose has been...
reported elsewhere [4]. Following are the steps involved in the preparation of alumina–silica gel with the pores impregnated with nickel chloride and dextrose:

Step 1. Required quantity of aluminium isopropoxide (98% +, Eastgate White Lund, England) is added to double distilled water in the molar ratio of 1:100 and hydrolysis of the former is carried out at a temperature of 80°C under constant stirring. As a result boehmite is precipitated according to the following reaction:

$$\text{Al(OCH}_3\text{H}_2)_3 + 2\text{H}_2\text{O} = \text{AlO(OH)} + 3\text{C}_2\text{H}_3\text{OH} \quad (1)$$

Step 2. Nitric acid (71%, International Chemicals, India) — 0.13 mole per mole of boehmite is added to boehmite and left for peptisation at 90°C under constant stirring for 3 h to get a clear sol.

Step 3. 5 cc of TEOS (98% +, Merck, Germany) is added to 5 cc of absolute alcohol (99.7%, Zuhai, China) under constant stirring.

Step 4. 5 cc of absolute alcohol and 5 cc of double distilled water are mixed under constant stirring. To this, measured quantity of nickel chloride and dextrose are added and a homogeneous solution is obtained.

Step 5. Solution from step 4 is added drop wise under constant stirring to solution from step 3 to get homogeneous solution of TEOS, water, alcohol, nickel chloride (99.91%, s.d-fine chemicals, India) and dextrose (99.8%, Luba Chemie, India). TEOS/water/alcohol :: 1:1:2 is then maintained in the resultant solution.

Step 6. Solution from step 2 is mixed thoroughly with the solution of step 5 under constant stirring at room temperature to get alumina–silica gel containing nickel chloride and dextrose.

Step 7. The mixed solution is left for gelling. The gel formation has taken place in a day.

Step 8. For alumina gel, the sol from step 2 is allowed to cool to room temperature and then required quantity of nickel chloride and dextrose are added under constant stirring till the solution becomes homogeneous. It is then left at room temperature for 7 days for gellation.

Step 9. All gels are dried before subsequent reduction at elevated temperature.

Reduction treatment of the gel samples have been carried out under flowing nitrogen atmosphere in a tube furnace at 900°C for half an hour with an accuracy of ±1°C, temperature maintained by PID controller. The same time and temperature have been used for the reduction of all the gel samples.

The reduced samples are ground to pass through 300 mesh. XRD patterns have been taken by using Cu kα, radiation in SEIFERT C3000 diffract meter. The ground reduced gel sample is dispersed in acetone and a few drops are then taken on to the carbon-coated grid. The electron beam can be transmitted through the wedge shaped fine particles left on the grid after the acetone is dried up. The TEM micrograph and selected area diffraction (SAD) pattern are taken by using Transmission Electron Microscope (JEOL JEM 200 CX, operating voltage 160 KV)

3. Results and discussion

The XRD patterns have been shown in Figs. 1–5. Different phases corresponding to different peaks have been indicated in Figs. 1–5. From these figures we observe that α-Al₂O₃ and γ-Al₂O₃, θ-Al₂O₃, δ-Al₂O₃, NiO and metallic nickel are present in different heat treated samples with different forms of Al₂O₃ present in all the gels. It is observed that for samples corresponding to pure alumina and alumina/silica ratio 1:0.5 (see Figs. 1 and 2) no nickel peak has been observed. This means in these samples nickel chloride has not been reduced. Gelling of alumina is known to occur by hydroxyl bonding of boehmite [14]. On heating to 900°C it is believed that the weak hydroxyl bonds gave away and the structure gets open precluding any possibility of in situ reduction as follows:

$$\text{CuH}_{12}\text{O}_6 \rightarrow 6\text{C} + 6\text{H}_2\text{O} \quad (2)$$

$$6\text{H}_2\text{O} + 6\text{C} \rightarrow \text{CO} + \text{H}_2 \quad (3)$$

$$\text{NiCl}_2 + \text{H}_2 \rightarrow \text{Ni} + 2\text{HCl} \quad (4)$$

When the molar ratio of silica and alumina becomes more than one, the matrix is held by strong Si–O–Si bond which remains unbroken at 900°C thereby ensuring stable matrix with nano sized pores. Hydrogen generated in situ through reactions (2) and (3) cannot immediately escape and takes part in the reduction of nickel chloride contained in the pores. The detailed reduction mechanism has been reported earlier [4]. As the amount of silica increased beyond 50% the intensity as well as the number of peaks corresponding to metallic Ni increases (Figs. 3–5). This indicates that higher the silica, better the rigidity of the matrix and this in turn helps in situ reduction process. The average particle size of metallic nickel has been calculated by the following relation:

$$t = 0.9λ/B \cos θ_b \quad (5)$$

where \(t\) is the average particle size in Å, \(B\) the width of peak at half the peak height in radian, \(λ\) the wave length in Å and \(θ_b\) is the Bragg angle in degree. The calculated particle size of metallic nickel for systems with alumina/silica molar ratio of 1:1, 1:2 and 1:4 are 10, 13 and 19 nm, respectively. This increase in size of the metallic nickel seems to arise from the increased amount of nickel due to the increase in silica content in alumina–silica system. Figs. 6 and 7 show the typical SAD pattern and TEM micrograph of the heat treated gel containing alumina and silica in the ratio of 1:4. The computed \(d_{obs}\) values from SAD pattern (Table 1) also corroborates the presence of metallic Ni and alumina phase.
Fig. 1. X-ray diffractogram of pure alumina gel after reduction.

Fig. 2. X-ray diffractogram of alumina–silica gel (molar ratio 1:0.5) after reduction.
Fig. 3. X-ray diffractogram of alumina–silica gel (molar ratio 1:1) after reduction.

Fig. 4. X-ray diffractogram of alumina–silica gel (molar ratio 1:2) after reduction.
It is also noted that the particle size estimated from the TEM micrograph is 11 nm in comparison to the size (19 nm) computed from XRD analysis.

4. Conclusions

(i) Incorporation of silica in alumina gel matrix is

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**Table 1**

TEM observation of alumina–silica gel (molar ratio 1:4)

| $d_{\text{iat}}$ values computed | $d_{\text{iat}}$ values standard |
|----------------------------------|----------------------------------|
| 2.592                            | Ni                               |
| 1.650                            | $\gamma$-Al$_2$O$_3$             |
| 1.252                            | 2.562                            |
| 1.083                            | 1.621                            |
|                                  | 1.246 (220)                      |
|                                  | 1.062 (311)                      |
necessary for reduction of metal salts by in situ generated hydrogen.

(ii) Al₂O₃–SiO₂–Ni nanocomposites can be prepared by in situ reduction if silica:alumina (molar ratio) is in excess of 1:1.

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