Incorporation of cobalt and nickel metal nano-particles in nano-grain zirconia film matrix by solution route*

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Abstract. Precursor solutions of cobalt/nickel incorporated nano-grain zirconia films were prepared from aquo-organic solutions of zirconium oxychloride octahydrate and corresponding transition metal nitrate. The films were deposited onto silica glass substrate by the dipping technique. Annealing was made at different temperatures from 450°C to 1200°C $\pm$ 5°C in air atmosphere. The range of thickness of the films baked at 450°C was 1800–1870 Å. For cobalt system Co₃O₄ was formed initially at 450°C which gradually transformed to alpha cobalt and next to cubic cobalt along with a non-stoichiometric compound (Zr_{0.71}Co_{0.23}O_{0.06}) with increasing annealing temperature. On the other hand, for nickel system nickel metal of nano-size was observed in the nano-grain zirconia film matrix at 450°C. By increasing annealing temperature to 1200°C, a compound, ZrNi₄O, was formed which was found to be stable for ~ 30 days.

Keywords. Nano-grain zirconia; nano particles of cobalt and nickel metals; sol-gel.

1. Introduction

The metal elements of the first transition series have partially filled 3d-orbital either in the ground state of the free atom (all except Cu) or in one or more of their chemically important ions (all except Sc) and these exhibit variable valencies in their oxides, complexes and also in some rare cases in free ions (Bogus and Kevan 1989). It is known that the metal oxides and/or the lower valent metal ions or metals either in pure state or incorporated in a suitable matrix have implications for their applications as promising catalysts (Ghosh and Kevan 1990), non-linear optical materials (Ando *et al* 1995) and optical filters (Ulrich 1988). Moreover, there are wide applications of M(Co/Ni/Cu)/zirconia or yttria stabilized zirconia cermets traditionally used as anodes in the solid oxide fuel cell configuration (Echigoya *et al* 1996; Sammes *et al* 1996). Zeng *et al* (1995) and Zeng and Shi (1995) have studied nickel impregnated zirconia system by the sol-gel technique in detail which involved different valence states of nickel although the valence state of the starting nickel metal ion was 2.

The generation of lower valent oxides and/or ions/or generation of metals is usually done by hydrogen reduction (Ghosh and Kevan 1990), or by the irradiation (Bogus and Kevan 1989) of higher valence states. It has already been established that zirconium oxychloride octahydrate derived nano-grain zirconia film possesses oxygen deficiency in the zirconia network (Jana and Biswas

1997). Such oxygen deficient centres are so active that these can trap electrons (Liu *et al* 1995). If divalent transition metal ion be incorporated into the precursor solution of zirconia film, then it may be expected that the trapped electrons in the developed zirconia film matrix may reduce the transition metal ion. And in this case some special properties may be developed in the film.

Moreover the oxygen deficient zirconia may yield (Jana and Biswas 1997) partially stable ZrO₂–Zr₂O₃ similar to the partially stabilized zirconia (Hillert 1991). Hence, both the phenomena, oxygen deficiency and partial stabilization of zirconia may yield Co/Ni/Cu cermets in thin film form in relatively easy way. Hence, in this work only Co and Ni have been considered for the study of the metal incorporated zirconia films.

2. Experimental

2.1 Preparation of precursor solutions

The precursor solutions were prepared by using requisite amount of hydrated zirconium salt (e.g. zirconium oxychloride octahydrate), transition metal salts (e.g. cobalt nitrate hexahydrate), organic solvents (e.g. ethanol, 2-butanol) and complexing or polymeric agent (e.g. glacial acetic acid). The atomic ratio of Zr : M (M, Co/Ni) in the solutions was 1 : 1. Two solutions (types I and II corresponding to zirconium and transition metal salts) were initially prepared separately by dissolution in suitable solvents and addition of a complexing agent if necessary and next, these two solutions were mixed and stirred with a magnetic paddle for about 30 min. These solutions were aged for 120 h and used as precursors of the films. The

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flow chart (figure 1) displays a pictorial view of preparation of precursor solutions.

2.2 Deposition of films

The films were deposited on cleaned (Atta *et al* 1990) pure silica glass substrate using the above aged precursor sols/solutions. These were done by the dipping technique with a withdrawal speed of 18 cm/min. A solution layer was formed on both sides of the glass substrate. Freshly

prepared solutions resulted in patch-like (inhomogeneous) films but after ageing for ~ 120 h, homogeneous films were developed. After dipping, the coated samples were placed in an air oven and heated at 100°C for 30 min and then put into a furnace for baking at $450^\circ \pm 5^\circ\text{C}$ in air atmosphere when oxide films were usually generated. Next these were annealed at different selected higher temperatures (600°, 730°, 940° and $1200^\circ \pm 5^\circ\text{C}$) in the same atmosphere. The duration of annealing was 30 min in each case.

2.3 Characterization of films

Absorption spectra of the films were recorded by using Shimadzu UV-VIS-NIR spectrophotometer (model, UV-3101PC) and paramagnetic properties of the films were measured at room temperature by utilizing a JEOL, JES-RE1 spectrometer operating in the X-band condition with 100 kHz field modulation. DPPH standard marker was used to calibrate ESR parameters. Crystallinity of the films were checked by a X-ray diffraction unit (Philips PW 1730) employed with nickel filter CuK_α radiation. A JEOL, JEM-200CX, transmission electron microscope (TEM) was employed to analyse the microstructure of the films. The thickness of the films was measured by stylus method (Sloan, DEKTAK).

3. Results and discussion

Cobalt nitrate incorporated zirconia precursor sol/solution layer deposited on silica glass substrate transforms to gel on air drying. When it is heated to around 450°C in an electrical furnace most of the organics are evaporated off and/or decomposed to generate oxide film. In this case, it is expected from literature (Mellor 1935) that at around 300°C formation of Co_3O_4 started and at 450°C considerable amount of Co_3O_4 was formed as evident from the

Figure 1. Flow chart of preparation of precursor for film formation.

Figure 2. Absorption spectra of cobalt incorporated nano-grain zirconia films in the visible region.

appearance of characteristic absorption band (~ 730 nm) (Ando *et al* 1995) in the visible spectra of the film which became prominent (figure 2) for the sample annealed at 730°C . It was observed from X-ray diffractograms (figure 3) of the samples annealed at different higher temperatures, viz. 600° , 730° and 940° , that a mixture of α -cobalt ($2\theta = 37^\circ$) and cubic spinel Co_3O_4 ($2\theta = 37^\circ$) phases were possibly formed at 730°C . The α -cobalt transformed to cubic form of cobalt at 940°C . It is also interesting to note that a non-stoichiometric compound, $\text{Zr}_{0.71}\text{Co}_{0.23}\text{O}_{0.06}$, was also formed ($2\theta = 38^\circ$, strong and 65° , weak) at this high temperature (1200°C). This probably happened during the transformation of alpha-cobalt to cubic cobalt when the liberated cobalt metal possibly reacted with the host material, zirconia. As the cobalt metal itself is a reducing agent, it reduced zirconia which instantaneously reacted with some of the residual cobalt metal and formed the above non-stoichiometric compound. The TEM picture (figure 4a) of a typical sample, annealed at 730°C shows the clusters of cobalt metal which disappeared (not shown here) at 1200°C possibly due to evaporation of cobalt metal.

On baking the nickel incorporated zirconia sol/solution layer deposited on silica glass it was observed that in the

Figure 3. X-ray diffractograms of the samples prepared by annealing the cobalt (A, 600°C ; B, 730°C and C, 940°C) and nickel (D, 1200°C) incorporated zirconia films (I, II, III, IV and V represent the characteristic 2θ peaks of the species, *t/c*-zirconia, α -cobalt and/or cubic spinel Co_3O_4 , $\text{Zr}_{0.71}\text{Co}_{0.23}\text{O}_{0.06}$ cubic cobalt metal and ZrNi_4O respectively).

Figure 4. TEM micrographs of cobalt incorporated (a) annealed at 730°C and nickel incorporated (b) annealed at 450°C nano-grain zirconia films.

Figure 5. Ultraviolet spectrum (a) and ESR spectrum (b) of 450°C annealed nickel incorporated nano-grain zirconia films.

developed oxide film the Ni(II) was partially reduced to metallic nickel as evidenced from the surface plasmon resonance (SPR) of Ni(0) (metallic nickel) at ~ 3.6 eV (Isobe *et al* 1995) in the ultraviolet spectrum (figure 5a) of the 450°C annealed sample. The ESR spectrum (figure 5b) of the same sample showed a broad resonance signal with $g = 2.23$ and peak to peak field ~ 800 G which might be attributed to Ni(0) (Bonnevot *et al* 1987; Bogus and Kevan 1989). Its formation might also be due to reduction of Ni(II) occurred by the trapped electrons present in the oxygen deficient centres of nano-grain zirconia (Jana and Biswas 1997). In addition a compound, ZrNi_4O was also found to form in the case of 1200°C annealed sample as evident from its X-ray diffractogram (figure 3). The possible reason for formation of this species may be similar as described in the case of cobalt system. The TEM picture (figure 4b) of this film showed dark particles which might be due to Ni(0) and/or oxides of nickel.

5. Conclusion

This work reveals that starting with Co and Ni metal salts, corresponding metal may be incorporated in a suitable oxide matrix like zirconia if the grain/particle size of the host material be in the nano-size range. Although the content of metal was not quantified in this work but the knowledge of this would enlighten the future prospects on synthesis of metal cermets which are essential for SOFC devices.

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