Nanoporous Ag template from partially sintered Ag–Zn compact by dezincification

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Abstract. A novel approach is followed to successfully fabricate nanoporous thin Ag template using partial sintering of elemental Ag and Zn (both have 99.9% purity) and subsequent dezincification. The starting materials for dezincification are partially sintered Ag–Zn aggregates (2.5, 5 and 10 wt% Zn). Partial sintering is done in order to achieve only interfacial bonding with the aim to maintain maximum potential difference between Ag and Zn particles during dezincification process in 1 N HCl and 3.5 wt% NaCl solutions. Two different dissolution methods, namely, simple immersion for 45 days and electrochemical way (holding the sample at critical potential), are employed. Electrochemical polarization tests are carried out to determine the critical potential for subsequent chrono-amperometry. X-ray diffraction, optical microscopy, scanning electron microscopy and energy dispersive X-ray spectroscopy are carried out to examine microstructural evolution, size, distribution and nature of pores in sintered aggregate as well as in template.

Keywords. Sintering; chrono-amperometry; porosity; dezincification; SEM; EDAX.

1. Introduction

Noble metals (Huang and Sun 2004; Yeh *et al* 2006; Jia *et al* 2007), such as Au, Ag, Pt and Cu, are very useful in applications like separation membranes in fuel cells, fluid filters, electrodes, structural materials due to light weight, catalyst supports, heat exchangers, impact energy absorbers, adsorbants and flame arresters. This is because of their unique properties of very high surface area as well as suitable stiffness (Rintoul *et al* 1996; Bond and Thompson 1999; Joo *et al* 2001; Ding and Erlebacher 2003; Katagiri and Nakata 2003; You *et al* 2003). On the other hand, dealloying is a commonly noticed corrosion process in Cu–Zn (Pickering and Wagner 1967), Cu–Au (Fritz and Pickering 1991; Moffat *et al* 1991) and Ag–Au (Forty 1979; Erlebacher *et al* 2001), where selective chemical or electrochemical dissolution of a component of an alloy occurs even under normal atmospheric conditions. Fabrication of novel materials like Au (Li and Sieradzki 1992), Cu (Hayes *et al* 2006), Ag (Qiu *et al* 2011), Ni (Pavlik and Adkins 1946), Ti (Wada *et al* 2011), Pt (Pugh *et al* 2005) and stainless steel (Chen and Sieradzki 2013) by dealloying has recently gained enormous attention due to their easy and effective processing route and ability to manipulate the final porous structure. On the other hand, different mechanisms of dezincifica-

tion have been proposed by various researchers (Deakin *et al* 2004) based on dissolution of active metal ions (Pickering and Wagner 1967), inter-diffusion (Pickering and Wagner 1967) and percolation theory (Sieradzki and Newman 1986; Newman *et al* 1988). Previous attempts on preparation of noble porous metallic sheets are concentrated on electro-deposition (Cherevko *et al* 2010), lyotropic liquid crystalline phases (Attard *et al* 1997; Bartlett *et al* 2002), foaming techniques using gas as blowing agent (Banhart 2001) and colloidal crystal templating (Velev and Kaler 2000). Several powder metallurgy techniques including loose powder sintering, slurry foaming and fibre metallurgy have also been tried for the production of high porosity metals (Shapovalov 1994). Even unidirectional solidification route under hydrogen gas has also been employed to achieve fine porous Cu (Nakajima *et al* 2001). But all these routes require extreme control, and are not easily available. Thus, dealloying route is found to be easy, yet successful route for fabrication of metals. So, fabrication of porous materials using sintering and dealloying route is quite a novel approach. Only disadvantage of this route is that the final amount of porosity is restricted to the amount of dissolution of the 2nd phase up to a certain limit decided by equilibrium phase diagram. Recently, Zhang *et al* (2012) have shown that melt-spun Zn–Ag alloy ribbons of varied composition can form ~50 µm thick dealloyed Ag sheet in NaCl and HCl solutions. The idea of producing porous materials using dissolution route from partially sintered

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aggregates have never been tried previously. Recently, the present authors have made a successful attempt to make porous Cu template from partially sintered Cu–Zn aggregate by dealloying (dezincification) after immersion in NaCl and HCl solutions (Mandal *et al* 2013). Further, this route does not provide any complicity as it only involves simple powder mixing using ball milling, partial sintering and electrochemical studies (simple immersion or chrono-amperometry). Similar novel approach (mechanical mixing of pure Ag and Zn powders in ball mill, partial pressureless sintering, dealloying by immersion as well by chrono-amperometry) has been followed in the present work for the first time to successfully produce Ag template. Potentiodynamic polarization and chrono-amperometry studies have been performed further to modify the final microstructure of Ag template.

2. Experimental

According to the Ag–Zn binary phase diagram (shown in figure 1 (Massalski 1986)) and considering the solid solution range of Ag and Zn, three compositions were chosen, such that vigorous formation of intermetallic compounds might be avoided at room temperature as well as at elevated temperature. Electrolytically prepared Zn powder (99.9% pure, density 7.13 g/cm³) and Ag powder (99.5% pure, density 10.46 g/cm³) were then milled in a planetary ball mill (Fritsch Planetary Ball Mill, Pulverisette 5 PM400) at 200 rpm for 45 min to prepare three sets of powders having compositions Ag–2.5 wt% Zn, Ag–5 wt% Zn and Ag–10 wt% Zn. Milling was carried out using tungsten carbide vials and tungsten carbide balls of 10 mm diameter in a dry atmosphere with a ball to powder ratio of 10:1. Compaction had, then, been done for each of the samples using 10 mm stainless-steel die for 15 s

under uni-axial load of 4.5 kN. The green densities of the compacts were then measured, and relative densities with respect to the theoretical density were assessed. Sintering was then done in low vacuum (10^{−2} mbar) at two different temperatures of 450 and 500 °C for 15 min to restrict oxidation of Ag. The samples were then furnace cooled up to 150 °C followed by air cooling to room temperature. X-ray diffraction (XRD) using CuK α radiation ($\lambda = 0.15418$ nm) was carried out after ball milling and sintering. The peaks were compared with the standard peaks using PCPDFWIN and X'pert Highscore plus software. Density of the sintered pellets was measured by the Archimedes method following ASTM B962-08 standard. The pellets were first weighed in air using a weighing balance cum density kit (Mettler Toledo), and then, they were soaked with oil to close the open pores on the surface. The soaked samples were weighed inside water. Direct density values were obtained from the machine. Following formula was used for the calculation of sinterability of the pellets:

$$\text{Sinterability} = \text{experimental density/theoretical density.}$$

Scanning electron microscopy (SEM) (Model SEM ZEISS EVO 50) was carried out for micro-structural characterization of the sintered samples. Metallographic samples were prepared by polishing on 400–2000 grit SiC paper, followed by cloth polishing using 5 μ m alumina. SEM equipped with energy dispersive X-ray spectrometer (EDS) was used for compositional analysis (point as well as elemental mapping) to study the degree of uniformity and distributions of the different constituents in sintered samples. Bulk hardness was measured using the Vickers indenter by applying a load of 50 g for 10 s, and minimum 20 indentations were recorded for each sample at random places in order to have a representative average value of hardness.

For dezincification studies, 0.5 mm thick discs were sliced out from sintered pellets of 10 mm diameter. Direct immersion tests were carried out on Ag–Zn samples sintered at 500 °C by suspending each of the fine-polished pellet samples (up to 1600 grit size) in separate conical flasks containing 250 mL of two different types of non-agitated solutions 1 M HCl (pH 0.47) and 3.5 wt% NaCl (pH 7.2) for 45 days maintained at room temperature (25 °C). The samples were then properly cleaned ultrasonically in acetone for 10 min. Microstructural analysis was then performed in SEM equipped with EDS for the characterization of size, distribution and nature of pores after dezincification.

Electrochemical studies, including open-circuit polarization (OCP) measurements, potentiodynamic polarization and finally chrono-amperometry, were carried out in conventional electrochemical flat bottom cell using a potentiostat (Model 2263, Princeton Applied Research, USA) at room temperature in an open ambient condition. Platinum gauze was used as the counter electrode. The electrode potential was measured using a saturated calomel

Figure 1. Binary alloy phase diagram of Ag–Zn (Yeh *et al* 2006) and the position of the chosen Ag–Zn mixtures is shown in the figure with arrowhead.

electrode (SCE) as reference electrode ($E_{\text{SCE}} = 241 \text{ mV}$). The Ag–Zn pellets were directly used as working electrode. The electrolytes used were freshly prepared 1 M HCl (pH 0.49) and 3.5 wt% NaCl (pH 7.2). In order to avoid experimental errors, OCP and potentiodynamic measurements were repeated at least two times. For the potentiodynamic polarization measurements, the scanning rate was chosen to be 0.75 mV/s. The critical potentials for chrono-amperometry were chosen from the potentiodynamic studies of the partially sintered samples for fabrication of porous Ag pellets. The samples after chrono-amperometry were then properly cleaned ultrasonically in acetone for 10 min. Microstructural analysis was then performed in SEM equipped with EDS for the characterization of size, distribution and nature of pores after dezincification.

3. Results and discussion

Figure 2(a) and (b) shows the XRD patterns of pure Ag and Zn powders and the mixed Ag–Zn powders after ball milling, respectively. The ball-milled powders show distinct Ag peaks, whereas the Zn peaks are relatively weaker because only 2.5, 5 and 10 wt% Zn are present. The presence of distinct Ag and Zn peaks in the ball-milled powders shows that predominantly Ag and Zn are present in elemental form in the milled powders. However, the patterns show some additional peaks confirming the formation of small fraction of AgZn (cubic), Ag_5Zn_8 , AgZn_3 and AgZn (hexagonal) phases. This suggests that there is a possibility of reaction between Zn and Ag particles at the powder particle interfaces during low-energy ball milling.

Figure 2. X-ray diffraction patterns of (a) pure Ag and Zn elemental powders and (b) ball-milled powders, sintered Ag–2.5 wt% Zn, Ag–5 wt% Zn and Ag–10 wt% Zn at (c) 500 °C and (d) 450 °C.

Figure 2(c) and (d) shows the XRD patterns from the sintered Ag–Zn aggregates at 500 and 450 °C, respectively. These patterns clearly show that with increase in Zn content as well as with increase in sintering temperature, new peaks appear apart from the elemental peaks. However, elemental peaks of pure Zn and Ag still persist suggesting that there are reactions between Ag and Zn at the particle boundaries. Formation of intermetallics like AgZn_3 , Ag_5Zn_8 (cubic), AgZn (cubic) and AgZn (hexagonal) occurs in the sintered samples too.

Figure 3(a) shows the variation of green densities of the compacted samples and that of the sintered pellets as a function of Zn content. The density increases with decrease in Zn content, suggesting better sintering, although the rate of change in density is almost constant. Figure 3(b) shows the corresponding plot of variation of sinterability as a function of Zn content. The density of the sintered sample is maximum (9.04 g/cm^3) at the highest sintering temperature (500 °C) and minimum Zn content (2.5 wt%). On the other hand, density is minimum

Figure 3. Variation of (a) density and (b) sinterability of the green compact and sintered pellets as a function of composition.

Figure 4. Scanning electron micrographs of (a) Ag–2.5 wt% Zn, (b) Ag–5 wt% Zn and (c) Ag–10 wt% Zn samples sintered at 450 °C.

(8.41 g/cm³) at 450 °C with maximum Zn content (10 wt%). This is due to the fact that the density of elemental Zn (7.14 g/cm³) is much lower than that of Ag (10.49 g/cm³), and upon mixing, the density decreases due to the presence of low-density Zn. Moreover, Zn might have evaporated also during sintering, leading to porosity.

Figure 4(a)–(c) shows the scanning electron micrographs in the secondary electron imaging mode (SE) of Ag–2.5 wt% Zn, Ag–5 wt% Zn and Ag–10 wt% Zn, sintered at 450 °C, respectively. The dark phases indicate the presence of Ag-rich phases, while the bright phases indicate Zn-rich phases. Zn is distributed throughout the matrix in the interface regions of Ag particles in all the samples. With increasing Zn content, the Ag-rich regions tend to increase in size. Very-fine microstructure is observed in Ag–2.5 wt% Zn sintered at 450 °C. Coarse-grained microstructure is found in case of Ag–10 wt% Zn. This could be associated with composition-assisted grain boundary migration of Ag grain in contact with Zn (Balluffi and Cahn 1981). However, the present paper presents more on dealloying and associated porous structure. From EDS area mapping, the volume fraction of

Zn-rich phase is found to be 2.04%, 4.29% and 9.1% in cases of Ag–2.5 wt% Zn, Ag–5 wt% Zn and Ag–10 wt% Zn, respectively. The remaining Zn could have evaporated during sintering. However, near about 90% Zn is retained in each aggregate irrespective of composition after sintering. There could be loss of Zn during milling also. Figure 5 shows the elemental mapping of zinc and silver carried out on Ag–10 wt% Zn sintered at 450 °C. The EDS superimposition on the original microstructure shows Ag-rich and Zn-rich regions clearly. The elemental mapping showing distribution of Ag-rich and Zn-rich phases in Ag–10 wt% Zn after sintering at 500 °C are shown in figure 6. The large grains are mostly in Ag-rich regions, whereas Zn is found to be present mostly in grain boundary regions.

Figure 7(a) and (b) shows the plots describing the variation of the Vickers hardness with increase in Zn content and sintering temperatures, respectively. The Vickers hardness shows an increasing tendency with decreasing Zn content as well as increasing sintering temperature, and it is highest (97.4 VHN) for Ag–2.5 wt% Zn sample sintered at the highest sintering temperature (500 °C). It is also noticed that the hardness of Zn-rich regions is much lower than Ag-rich regions. It is due to increase in Zn

Figure 5. Elemental mapping showing distribution of Ag-rich and Zn-rich phases in the Ag–10 wt% Zn sample sintered at 450 °C.

Figure 6. Elemental mapping showing distribution of Ag-rich and Zn-rich phases in the Ag-10 wt% Zn sample sintered at 500 °C.

Figure 7. Variation in bulk hardness (Vickers) with respect to Zn content in sintered Ag-Zn samples.

content, and there is a sharp decline in the hardness of the samples. With an increase in sintering temperature, better interparticle bonding occurs leading to a higher hardness value.

Scanning electron micrographs (figure 8a and b) show morphology of the surface of Ag-10 wt% Zn sintered at 500 °C after immersion in 3.5% NaCl and 1 M HCl, respectively, for 45 days. EDS analysis has been performed at several points in order to obtain the amount of Ag and Zn. Table 1 shows the data of EDS analysis marked by points A, B and C as shown in figure 8(a) and (b). Very fine pores ranging from 200 nm to 1 mm have formed in the Ag-10 wt% Zn sintered at 500 °C sample after dissolution in 1 M HCl sample (figure 8b). But, the morphology after dissolution in 3.5% NaCl seems to be somewhat different (figure 8a), showing inhomogeneous distribution of large and fine sized pores. The EDS data further shows that oxide content is very low in all the samples even after dissolution in aerated solution, and the dissolution of Zn is quite pronounced in both HCl and NaCl solutions (table 1). Scanning electron micrographs (figure 8c and d) show the morphology of the surface of the Ag-5 wt% Zn sintered at 500 °C after immersion in 3.5% NaCl and 1 M HCl, respectively, for 45 days. The EDS analysis at the points marked in figure 8(c) and (d) is presented in table 1. In case of the Ag-5 wt% Zn sample immersed in 3.5% NaCl, the range of pore size reduces, and homogeneous porous microstructure is

Figure 8. Scanning electron micrographs of the Ag–10 wt% Zn sample sintered at 500 °C after immersion (a) in 3.5% NaCl and (b) in 1 M HCl for 45 days; and scanning electron micrographs of Ag–5 wt% Zn sample sintered at 500 °C after immersion (c) in 3.5% NaCl and (d) in 1 M HCl for 45 days.

Table 1. Compositional analysis (EDS) at the points marked in the micrographs of the corroded surfaces of Ag–Zn samples sintered at 500 °C after immersion as shown in figure 8.

Composition	Corrosive used	Location of EDS spectrum	Ag (wt%)	Zn (wt%)	O (wt%)	Avg. pore size
Ag–10 wt% Zn	1 M HCl (figure 8b)	A	97.15	0	2.85	560 nm
		B	94.80	4.16	1.04	
		C	92.54	6.49	0.97	
	3.5% NaCl (figure 8a)	A	97.63	2.21	0.16	620 nm
		B	93.22	6.41	0.37	
		C	94.59	5.28	0.13	
Ag–5 wt% Zn	1 M HCl (figure 8d)	A	96.26	3.54	0.20	4.2 μm
		B	95.62	3.16	1.22	
		C	95.29	3.87	0.84	
	3.5% NaCl (figure 8c)	A	95.30	4.70	0	1.8 μm
		B	96.11	3.15	0.74	
		C	95.44	4.17	0.39	

observed with pore size varying from 200 to 500 nm (figure 8c). As compared to the Ag–10 wt% Zn samples, the dissolution of Zn is not that pronounced. Almost full Zn (5 wt%) with respect to the original sintered sample is retained at all the points. This may lead to the conclusion that selective dissolution of Zn has not occurred, and instead of that, overall dissolution from both Zn-rich and Ag-rich phases has taken place. But, in both the samples,

oxide film is not present even after dissolution in aerated solutions, and it may be due to the noble nature of Ag. Figure 9(a) and (b) shows the elemental mapping of zinc and silver carried out on Ag–10 wt% Zn sintered at 500 °C after immersion test for 45 days in 1 M HCl solution and 3.5% NaCl solution, respectively. Predominantly Ag is present, and the presence of little Zn is overshadowed by the Ag signals.

Figure 9. Mapping of the overall corroded surface area showing elemental distribution of Ag and Zn in the Ag–10 wt% Zn sample sintered at 500 °C and immersed in (a) 1 M HCl and (b) 3.5% NaCl for 45 days.

Since the chemical response, i.e. evolution of pores is quite pronounced in immersion tests, there is a possibility that better results, i.e. homogeneous nanopores may be obtained on performing electrochemical experiments. The main idea behind this objective is that if the sample surface is exposed to the electrolyte at a stipulated potential, such that the potential is quite higher than the stability range of Zn, then controlled porosity can be obtained and the pore size can also be manipulated. Potentiodynamic polarization tests have thus been conducted to determine the critical potential and finally, chrono-amperometric studies have been conducted to obtain the final porous structure.

Figure 10(a) and (b) shows the potential vs pH (Pourbaix diagram) of Ag and Zn system, drawn to the same scale, respectively (Pourbaix 1966). Comparing the range of stability of elemental Ag (standard electrode potential 0.799) and Zn (standard electrode potential 0.762), it can be considered that elemental Ag is retained in the electrolyte even at much higher voltages than that of Zn. Thus, it can be assumed that the re-deposition of Ag takes place at a much lower potential than Zn, whereas selective

Figure 10. E -pH diagram of (a) Ag and (b) Zn drawn to same scale (You et al 2003).

dissolution of Zn is inevitable at higher potentials up to 0.799 V. The Pourbaix diagram further explains that pH of the electrolyte is very important since at higher pH, the stability of Zn further decreases and oxidation of Zn is likely to occur instead of selective dissolution. For this reason, low pH solution (1 M HCl in the present case) and neutral solution (3.5% NaCl) are chosen for performing the dissolution studies. The potentiodynamic polarization studies were conducted after stabilizing the open circuit potential (OCP) of the prematurely sintered Ag–Zn aggregates in 1 M HCl and 3.5% NaCl for 60 min.

The corresponding potentiodynamic polarization plots of the Ag–Zn aggregates are shown in figure 11(a) and (b) in 1 M HCl and 3.5% NaCl, respectively. Critical

potentials between the onset of transpassive and the passive zones on the anodic region are chosen for the corresponding samples, so as to facilitate further potentiostatic polarization studies at that critical potential, which may result into controlled porous structure. Table 2 shows all the critical potentials for all the samples.

Figure 12(a) and (b) shows the chrono-amperometric curves of the sintered Ag–Zn aggregates held at corresponding critical potentials in 3.5% NaCl and 1 M HCl, respectively. Dealloying has occurred from a circular area of 6 mm diameter. Critical potentials (shown in table 2) are chosen from the corresponding potentiodynamic polarization plots and the samples are held at that potential for 3600 s. The corresponding changes in current density

Figure 11. Potentiodynamic polarization (Tafel plot) of sintered Ag–Zn samples in (a) 1 M HCl and (b) 3.5% NaCl.

Figure 12. Potentiodynamic polarization (Tafel plot) of prematurely sintered Ag–Zn aggregates in (a) 1 M HCl and (b) 3.5% NaCl. Chronoamperometric curves of the sintered Ag–Zn aggregates in (a) 3.5% NaCl and (b) 1 M HCl held at the corresponding critical potentials for different compositions.

Table 2. Critical potentials for different alloys obtained from potentiodynamic plots.

Corrosive used	Sintering temperature (°C)	Sample	Critical potentials (V)
1 M HCl	450	Ag–2.5 wt% Zn	0.2
		Ag–5 wt% Zn	0.1
		Ag–10 wt% Zn	0.15
	500	Ag–2.5 wt% Zn	0.1
		Ag–5 wt% Zn	0.2
		Ag–10 wt% Zn	–0.012
3.5% NaCl	450	Ag–2.5 wt% Zn	0
		Ag–5 wt% Zn	0.1
		Ag–10 wt% Zn	0
	500	Ag–2.5 wt% Zn	–0.05
		Ag–5 wt% Zn	–0.03
		Ag–10 wt% Zn	0.035

Figure 13. Scanning electron micrographs showing the microstructures of porous Ag through potentiostatically dealloying of the (a) Ag–2.5 wt% Zn, (b) Ag–5 wt% Zn and (c) Ag–10 wt% Zn samples sintered at 500 °C in 3.5% NaCl. Composition has been measured (using EDS) at the points marked A, B and C in the micrographs.

with respect to time for each of the samples are then plotted. It is observed that the onset of dealloying or dissolution of Zn has occurred very fast, and it is because, the chosen critical potential is quite above the stability range of Zn as observed in the Pourbaix diagram of Zn as shown in figure 10. In 3.5% NaCl, initially there is a sudden drop in current density (shown in figure 12a) within few seconds and then, the current density is again increasing reaching to a threshold current. Then, it becomes stabilized suggesting that complete depletion of Zn has taken place. But in 1 M HCl, the trend is quite different. The reason may be due to the enhanced acidic nature of

1 M HCl, which restricts the passivation on the Ag surface resulting into constant dissolution from both Ag and Zn components.

Figure 13(a)–(c) shows the scanning electron micrographs showing microstructures of surfaces of porous Ag templates after potentiostatic dealloying of the Ag–2.5 wt% Zn, Ag–5 wt% Zn and Ag–10 wt% Zn aggregates sintered at 500 °C in 3.5% NaCl, respectively, at the respective critical potentials (table 2). EDS analysis has been done at the points marked on the microstructures, and are shown in table 3. Fine pores are observed in some regions of the Ag–5 wt% Zn sintered at 500 °C. But the

Table 3. Compositional analysis (EDS) of the points shown in the micrographs of potentiostatically dealloyed surfaces of Ag–Zn samples sintered at 500 °C in 3.5% NaCl at the points marked in figure 13.

Corrosive used	Sintering temperature	Sample	Spectrum	Ag (wt%)	Zn (wt%)	O (wt%)	Avg. pore size (μm)
3.5% NaCl	500 °C	Ag–2.5 wt% Zn Figure 13(a)	A	97.13	2.01	0.87	0.98
			B	97.80	1.94	0.26	
			C	97.44	2.05	0.51	
		Ag–5 wt% Zn Figure 13(b)	A	99.84	0	0.16	1.6
			B	99.34	0.18	0.48	
			C	97.58	0	0.42	
		Ag–10 wt% Zn Figure 13(c)	A	95.68	3.43	0.89	0.86
			B	93.79	5.48	0.73	
			C	95.52	3.92	0.56	

Figure 14. Mapping of the overall dealloyed surface area showing elemental distribution of 100% Ag after potentiostatically dealloying of the Ag–5 wt% Zn sample sintered at 500 °C sample in 3.5% NaCl.

size and distribution of the pores are found to be inhomogeneous. It may be attributed to the fact that the mechanism of dissolution might have changed continuously with further dissolution, and the electron cloud formed at the electrolyte metal interface might have restricted further dissolution. On the other hand, a star-shaped microstructure is observed in Ag–2.5 wt% Zn sintered at 500 °C. Upon EDS analysis, it is found that dissolution of Zn is very minute in Ag–2.5 wt% Zn sintered at 500 °C, and almost full Zn is retained at every point. Better results of dealloying are obtained in Ag–5 wt% Zn and Ag–10 wt% Zn sintered at 500 °C. Upon comparison of all the micrographs at same magnification shown in figure 13(a)–(c), it is found that the microstructures after sintering have been retained with extensive dissolution of Zn in case of the aggregates Ag–5 wt% Zn and Ag–10 wt% Zn sintered at 500 °C (table 3). Figure 14 shows the EDS elemental mapping of the Ag–5 wt% Zn aggregate sintered at 500 °C after potentiostatic dealloying in 3.5% NaCl. No trace of Zn is found throughout the entire surface suggesting complete dezincification. Comparing table 4 and figure 14, it can be understood that the trace amount of Zn observed after doing point analysis (table 4) could be from the undersurface.

Figure 15(a)–(c) shows the scanning electron micrographs showing microstructures of surfaces of porous Ag templates after potentiostatic dealloying of the Ag–Zn sintered aggregates sintered at 450 °C in 3.5% NaCl at critical potentials as shown in table 2. EDS analysis has been done at the points marked on the microstructures, and are shown in table 4. The morphologies of three sample surfaces are quite similar in pattern, and different from those of sintered samples at 500 °C shown in figure 13. In the present case, the re-deposition of Ag forms finer globules for the sample of highest Zn content (Ag–10 wt% Zn). But the pore size is found to be the smallest for the Ag–2.5 wt% Zn samples. The average pore size (992 nm) is found to be the largest in the Ag–5 wt% Zn samples. From the EDS analysis at the points marked on the microstructure, it is found that almost complete dissolution of Zn has also occurred from the Ag–10 wt% Zn sample. Since, the initial Zn content is already very low (2.5%) in the Ag–2.5 wt% Zn sample, it cannot be analysed properly that how much Zn has really dissolved into the electrolyte upon dealloying.

In low pH acidic solution, i.e. in 1 M HCl, the morphology of the dealloyed surface is somewhat different. Scanning electron micrographs (figure 16(a)–(c)) show

Table 4. Compositional analysis (EDS) of the points shown in the micrographs of potentiostatically dealloyed surfaces of Ag–Zn samples sintered at 450 °C in 3.5% NaCl at the points marked in figure 15.

Corrosive used	Sintering temperature	Sample	Spectrum	Ag (wt%)	Zn (wt%)	O (wt%)
3.5% NaCl	450 °C	Ag–2.5 wt% Zn	A	97.48	1.87	0.65
			B	98.48	1.43	0.09
			C	99.52	0.41	0.07
		Ag–5 wt% Zn	A	99.56	0.28	0.16
			B	99.78	0	0.22
			C	98.89	0.16	0.95
		Ag–10 wt% Zn	A	98.79	0.41	0.88
			B	97.90	1.95	0.15
			C	98.39	1.28	0.33

Figure 15. Scanning electron micrographs showing the microstructures of porous Ag through potentiostatically dealloying of the (a) Ag–2.5 wt% Zn, (b) Ag–5 wt% Zn and (c) Ag–10 wt% Zn samples sintered at 450 °C in 3.5% NaCl. Composition has been measured (using EDS) at the points marked A, B and C in the micrographs.

Figure 16. Mapping of the overall dealloyed surface area showing elemental distribution of 100% Ag after potentiostatically dealloying of the Ag–5 wt% Zn sample sintered at 500 °C in 1 M HCl.

Table 5. Compositional analysis (EDS) of the points shown in the micrographs of potentiostatically dealloyed surfaces of Ag–Zn samples sintered at 500 °C in 1 M HCl at the points marked in figure 17.

Corrosive used	Sintering temperature	Sample	Spectrum	Ag (wt%)	Zn (wt%)	O (wt%)	Avg. pore size (μm)
1 M HCl	500 °C	Ag–2.5 wt% Zn Figure 17(a)	A	98.45	0.34	1.21	4.2
			B	97.87	1.84	0.29	
			C	97.53	2.11	0.36	
		Ag–5 wt% Zn Figure 17(b)	A	97.85	1.52	0.63	2.6
			B	96.42	2.78	0.8	
			C	97.11	1.88	1.01	
		Ag–10 wt% Zn Figure 17(c)	A	95.07	3.82	1.11	1.4
			B	96.36	3.41	0.33	
			C	95.79	4.08	0.13	

Figure 17. Scanning electron micrographs showing the microstructures of porous Ag through potentiostatically dealloying of the (a) Ag–2.5 wt% Zn, (b) Ag–5 wt% Zn and (c) Ag–10 wt% Zn samples sintered at 500 °C in 1 M HCl. Composition has been measured (using EDS) at the points marked A, B and C in the micrographs.

microstructures of the surfaces of porous Ag templates after potentiostatic dealloying of the Ag–2.5 wt% Zn, Ag–5 wt% Zn and Ag–10 wt% Zn aggregates sintered at 500 °C in 1 M HCl, respectively, at critical potentials (table 2). EDS analysis has been done at the points marked on the microstructures, and is shown in table 5. Discrete particles of Ag are re-deposited back on the matrix after dissolution. Thus, the mechanical integrity of the sample may be lost if the whole sample would have been exposed to the electrolyte for potentiostatic

dealloying. This effect is most visible in the Ag–2.5 wt% Zn sample. It is also very clear from figure 10 that there could be possibility of AgCl formation which would lead to complete dissolution of the sample. Particle sizes are found to be smallest for the Ag–10 wt% Zn sample. The composition at the points (marked in figure 16(a)–(c)) shows that some amount of Zn is retained in the particles and the composition profile follows a similar pattern in all the samples. Figure 17 shows the EDS elemental mapping of the Ag–5 wt% Zn aggregate sintered at

500 °C after potentiostatic dealloying in 1 M HCl. No trace of Zn is found throughout the entire surface suggesting complete dezincification. It also suggests that the trace amount of Zn observed after point analysis (table 5) is from the subsurface of the sample.

Figure 18 shows the SEM microstructure of porous Ag template obtained through potentiostatic dealloying of the Ag–10 wt% Zn sintered at 500 °C at 0.36 V vs SCE in 3.5% NaCl solution. Homogeneous very fine pores, the size ranging from 200 to 900 nm with an average pore size of 450 nm, are found over the entire region of the matrix. When the holding potential is reduced to 0.32 V, the microstructure obtained is much sharper with crystals of Ag being visible at higher magnification (shown in the inset). The corresponding SEM microstructure of porous

Figure 18. Scanning electron micrographs showing the microstructures of porous Ag template obtained through potentiostatically dealloying of the Ag–10 wt% Zn sample sintered at 500 °C at 0.36 V vs SCE in 3.5% NaCl solution. Inset shows a higher magnification image.

Figure 19. Scanning electron micrographs showing the microstructures of porous Ag template obtained through potentiostatically dealloying of the Ag–10 wt% Zn sample sintered at 450 °C at 0.32 V vs SCE in 3.5% NaCl solution. Inset shows a higher magnification image.

Ag template obtained through potentiostatic dealloying of the Ag–10 wt% Zn sintered at 500 °C at 0.32 V vs SCE in 3.5% NaCl solution is shown in figure 19. The EDS results (shown in figure 20) of the corresponding structure demonstrate that Zn has completely been leached out during potentiostatic dealloying from the sample Ag–10 wt% Zn sintered at 500 °C at 0.36 V vs SCE in 3.5% NaCl solution.

Thus, it is observed that potentiostatic dealloying is most effective in neutral 3.5% NaCl solution, and with increasing Zn content in solid solution range of phase diagram. The amount of dissolution is very high too. The actual mechanism of dissolution is not clear in immersion test. It is not clear whether selective dissolution of Zn has occurred, or dissolution–redeposition mechanism is active. On the other hand, since the holding potentials in the potentiostatic experiment lie always within the stability range of elemental Ag and quite above the stability range of Zn, it may be concluded that full dealloying of Zn from the matrix (confirmed from EDS mapping) has

Figure 20. Mapping of the dealloyed surface of Ag showing elemental distribution of Ag over the entire area obtained through potentiostatically dealloying of the Ag–10 wt% Zn sample sintered at 450 °C at 0.36 V vs SCE in 3.5% NaCl solution.

probably occurred following selective dissolution route. Moreover, the time taken is very less (only less than 3600 s). Further, less than 500 nm pores are obtained (figures 18 and 19), which are distributed homogeneously throughout the matrix in Ag–10 wt% Zn sintered at 500 °C in 3.5% NaCl. Even in immersion test, best dissolution of Zn has been obtained for Ag–10 wt% Zn samples in 3.5% NaCl (figure 13). Thus, neutral electrolyte (3.5% Zn) has proven to be better medium facilitating better dissolution than acidic solutions. Moreover, the present approach of partial sintering is considered because it has resulted in the formation of hard intermetallics at the Ag–Zn interfaces forming a network-like structure on one hand, and the presence of elemental Ag and Zn has facilitated selective leaching of the more active element (Zn in the present case) forming a network of porous Ag structure.

4. Conclusions

Fabrication of nanoporous Ag templates from partially-sintered Ag–Zn alloys, respectively, using dealloying or selective dissolution mechanism is successful. Low-energy ball milling for shorter time has prevented extensive alloying, and formation of intermetallic compounds. Partial sintering has also led to intermetallic compounds, preferably at the interface between Zn and Ag particles. Immersion tests have resulted into formation of pores, but these pores are inhomogeneous in size as well as in distribution. The 3.5% NaCl solution has contributed to better porosity with the level of inhomogeneity less than that in 1 M HCl. Moreover, for successful dealloying and formation of porous structures, higher Zn content is helpful. Chrono-amperometry tests have resulted into fine porous homogeneous microstructure with complete retention of the more noble metal Ag and complete dissolution of the active metal Zn.

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