

PAPER

[View Article Online](#)
[View Journal](#) | [View Issue](#)

Recrystallisation-accompanied phase separation in Ag–Fe and Ag–Ni nanocomposites: a route to structure tailoring of nanoporous silver†

Boris B. Bokhonov* and Dina V. Dudina

Cite this: *RSC Advances*, 2013, **3**, 12655Received 20th March 2013,
Accepted 3rd May 2013

DOI: 10.1039/c3ra41377b

www.rsc.org/advances

We present, for the first time, a preparation method of nanoporous silver by phase separation in nanocomposite Ag–Fe and Ag–Ni systems, which are metal pairs immiscible in both liquid and solid states. Conveniently using high-energy mechanical milling, we achieve uniform mixing of the metal grains at the nanoscale in the mixtures containing 50 vol.% Ag. When Fe and Ni grains dissolve in hydrochloric acid, they leave behind a nanoporous silver skeleton, in which the size of coherently scattering domains is larger than that in the starting nanocomposite before the phase separation, while the microstrain is reduced. We explain these effects by recrystallisation of silver through the dissolution–precipitation mechanism enabled by oxidation of silver by oxygen of ambient air and the concomitant formation of HAgCl₂ in the solution followed by its reduction by metallic Fe or Ni in a galvanic displacement reaction. The originality of the proposed synthesis is in the dual functionality of the Fe and Ni sacrificial phases acting also as reducing agents and opening up a new mechanism of microstructure tailoring of nanoporous silver. Selective dissolution of Spark Plasma Sintered Ag–Fe and Ag–Ni compacts retaining silver nanograins can be used to produce nanoporous silver membranes.

Introduction

Porous metallic materials represent a wide class of materials, which is currently a subject of extensive fundamental and applied research.^{1–3} Porosity is desired to reduce specific weight or impart functional or filtering properties to the material. Nanoporous noble metals are promising materials for catalysis,⁴ optical applications⁴ and electrochemical actuation.^{5,6} The uniform open porosity and interconnected pore channels are important structural features allowing transport of gaseous and liquid matter through nanoporous metals. The pore size and spatial distribution of pores in a material can be tailored using sacrificial components, which are leached out to leave behind a system of pores. The removed species are either elemental components of single-phase alloys (solid solutions or intermetallic compounds)^{1,3} or separate phases initially introduced or synthesized within a material making up a composite structure.^{2,7} The corresponding porosity-creating processes are dealloying and phase separation; the former is the removal of an element from a phase, while the latter is the

removal of grains or particles of a phase, leaving behind the other one, both initially comprising a composite. The difficulty associated with dealloying is the existence of concentration limits for the less-noble metals, which should be present in the solid solution above a certain percentage for the dealloying to occur.³ The phase separation alternative is free from such limitations as pores form as a result of removal of a phase from a composite rather than atoms from a solid solution. Removal of a template does not bring about shrinkage and, for this reason, the particles and compacts are not prone to crack formation rather typical of dealloying, in which shrinkage often accompanies the reorganization of the crystalline lattice. It is relatively easy to form an interconnected nanopore structure by compaction and free sintering of ceramic nanopowders.⁸ Rigid ceramic particles can form a porous compact through particle rearrangement without a change in the particle shape. However, in the case of metals, plastic yielding during compaction may not allow an interconnected pore structure to form. In order to make such a structure, a leachable pattern should be used to hold space during the compact formation.

Due to simplicity and flexibility, mixing of powders is an attractive method of producing precursors for the phase separation-based processing of porous materials. Interesting composite systems are offered by pairs of immiscible metals. They do not form compounds and the differences in their chemical properties are often enough to easily find a corrosive

Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Kutateladze str. 18, Novosibirsk, 630128, Russian Federation. E-mail: bokhonov@solid.nsc.ru; Fax: 7-383-332-28-47; Tel: 7-383-233-24-10

† Electronic supplementary information (ESI) available: Characterization of the Ag–Fe composites produced by milling/annealing and products of their reaction with hydrochloric acid. See DOI: 10.1039/c3ra41377b

environment to selectively dissolve one of them from the mixture. Two-phase composites combining immiscible metals at the nanometer scale are attractive as precursors for making nanoporous metals by free corrosion. For more than two decades, pairs of immiscible metals have been of particular interest to study the physics of metastable phase formation and elucidate mechanisms responsible for forced alloying.⁹ From the application viewpoint, immiscible metals have been a promising choice for making structural composites combining properties of two different materials, *e.g.* high electrical and thermal conductivities and high-temperature stability (Cu–W)¹⁰ or high hardness and low coefficient of friction (Co–Bi).¹¹ An interesting yet poorly developed area of materials science of immiscible metal pairs is their chemical reactivity toward a third party. In such reactions, despite the absence of interaction at the interfaces between the immiscible metals, their mutual influence during the reaction can play a major role in determining the nature of the reaction products and their microstructure.

Nanocomposites of immiscible metals can be obtained by mechanical milling,¹² which is a simple and versatile method suitable for making composites without any limitations of the volume ratio of the components. Micron-sized powders of metals can be used as raw materials for solid-state processing by mechanical milling. They are normally less expensive compared to nanopowders or metal-containing organic compounds used in the solution synthesis of nanoparticles, and are oxidized to a lesser extent than the corresponding nanopowders. The grain size of the metal components and their mutual distribution can be tuned by varying the time of milling, rotation speed of the milling vials, ball to powder weight ratio as well as by the use of different milling media and surfactant additives as process control agents. During milling, powder particles experience grinding, mixing and accumulate defects as they become trapped between the milling balls or a ball and the wall of the milling vial. Repeated fracturing and cold welding of the particles during mechanical milling gradually refines the microstructure of the milled mixture and improves its uniformity according to the model of the baker transformation.¹³

In the present study, we focus on the preparation of nanoporous silver by phase separation. In order to respond to the needs of a broad range of applications, such as substrates for Surface-Enhanced Raman Scattering,¹⁴ antibacterial materials¹⁵ and membranes,⁷ novel processing methods of nanoporous silver should be found relying on simple and inexpensive procedures and enabling fine tailoring of the microstructure. The preparation procedures of nanoporous silver by dealloying of Ag–Mg and Ag–Al alloys as well as the underlying porous structure formation mechanisms related to the phase composition of the corresponding alloys (the presence of intermetallics) have been presented by Ji *et al.*¹⁶ and Detsi *et al.*¹⁷ The phase composition of the precursor alloy has to be thoroughly controlled by selecting the element ratio and the temperature treatment schedule. For mixtures of non-reacting metals, these complications do not exist. In this

article, we describe, for the first time, a preparation method of nanoporous silver by phase separation in Ag–Fe and Ag–Ni nanocomposites obtained by high-energy mechanical milling. We suggest high-energy mechanical milling of elemental silver and iron or nickel powders as an easy preparation procedure of nanocomposites consisting of nanograins of both metals thoroughly intermixed with each other. Ag–Fe and Ag–Ni metal pairs are immiscible in both liquid and solid states; during mechanical milling, these alloy systems can form only limited metastable solid solutions. Solid solutions of nickel in silver are achievable by mechanical alloying with 0.84 at.% Ni dissolved in Ag, as was found by Wang *et al.*¹⁸ and up to 4.3 at.% Ni dissolved in Ag, as was estimated by Xu *et al.*¹⁹ The solubility of iron in silver is very scarce and confined to the presence of iron atoms in the grain boundary regions of silver and interphase boundary regions between silver and iron in a two-phase composite structure.^{20–22} Planning a phase separation process in Ag–Fe and Ag–Ni nanocomposites by selective dissolution, we did not aim at obtaining solid solutions between the metals by mechanical alloying, and, for that reason, we did not perform prolonged milling of the metal mixtures.

Mechanically alloyed Cu–Ag alloys as precursors for nanoporous silver have been used by Spassov *et al.*,²³ who employed selective dissolution of copper from the product of mechanical milling. Their approach, however, was principally different from ours, as Cu and Ag metals are miscible in the liquid state and upon mechanical milling they can form extended solid solutions such that selective dissolution of copper from the product of milling can be considered as a dealloying example. The key feature of our scheme is the use of metals having negligible solubility in silver.

Morphologically, the products of mechanical milling are normally powder agglomerates tens or hundreds of microns in size. The porous material produced by phase separation from the mechanically milled powders will largely inherit this particle size. Since many applications require a bulk porous body, we made a further step in the processing of nanoporous silver by producing a consolidated material from the milled powders and subjecting it to selective dissolution. In order to consolidate the composite agglomerates into a compact, we have selected Spark Plasma Sintering (SPS), which has attracted a lot of attention in the past two decades as a promising method of fast and effective densification of metallic and ceramic materials.²⁴ Based on the simultaneous application of electric current and uniaxial pressure to the sample, SPS offers high heating rates and sintering within shorter times and at lower temperatures than in conventional methods thereby minimizing grain growth and making it possible to produce nanostructured bulk materials from nanopowders. The feasibility of using a two-phase composite with an interpenetrating structure sintered by the SPS as a precursor for porous bodies has been earlier demonstrated by Kim *et al.*,²⁵ who employed electrochemical etching of TiB₂–Cu metal–ceramic composites to selectively remove copper and form a nanograin titanium diboride skeleton.

Experimental section

In this study, Ag–Fe and Ag–Ni binary mixtures containing 50 vol.% of Ag were prepared. Fe (99.9% purity, average particle size 5 μm), Ni (99.9% purity, average particle size 10 μm) and Ag (99.9% purity, average particle size 0.5 μm) powders were taken as raw materials. A high-energy planetary ball mill with water-cooled milling vials was used to prepare the nanocomposite mixtures. The powder mixtures were loaded in the milling vials in a glove box under an atmosphere of high-purity argon. The ball to powder weight ratio in all experiments was 20 : 1. Stainless steel vials and balls of 8 mm diameter were used. No process control agent was added during milling of the mixtures. The milling time was 60 min. Spark Plasma Sintering of the nanocomposite powders was carried out using a SPS Labox 1575 apparatus (Japan). A graphite die of 20 mm internal diameter and 50 mm external diameter and graphite punches of 20 mm diameter were used. The die wall was lined with a carbon foil. The temperature during the SPS was controlled by a K-type thermocouple NSF600 (CHINO) 1.6 mm in diameter placed in the die wall at a depth of 5 mm. The sample was heated at a rate of 100 $^{\circ}\text{C min}^{-1}$. The maximum SPS-temperature was 600 $^{\circ}\text{C}$. The sample was held at the maximum temperature for 0 min and then was cooled down to room temperature. At the beginning of the sintering cycle, a uniaxial pressure of 40 MPa was applied and kept constant through the sintering cycle. Porous silver was prepared from the powder nanocomposites and SPS-ed compacts by selective dissolution of Fe or Ni in 20 wt.% HCl aqueous solution. The X-ray diffraction (XRD) patterns of the powders and sintered specimens were recorded using a D8 ADVANCE diffractometer (Bruker AXS) with Cu-K α radiation. The size of coherently scattering domains and lattice microstrain were determined through Rietveld analysis of the corresponding XRD patterns performed using PowderCell 2.4 software.²⁶ The microstructure of the nanocomposite powders, SPS-ed compacts and nanoporous silver was studied by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) using a Hitachi Tabletop TM-1000 microscope. SPS-ed compacts were cut and polished to observe the microstructure on a cross-sectional view of the material.

Results and discussion

The products of mechanical milling for 60 min consist of dense composite agglomerates showing uniform intermixing of iron and silver or nickel and silver phases at the nanolevel (Fig. 1, a–b). The time of mechanical milling for preparing nanocomposite precursors was chosen based on a preliminary study of the microstructure evolution of the composite agglomerates with milling time. As exemplified in Fig. S1, ESI† the Ag–Fe agglomerates formed after 10 min of milling are large particles ranging from 200 to 400 μm , which still show micron-sized iron inclusions embedded in a finer-structured Ag–Fe matrix. As mechanical milling continues, mixing becomes more uniform and the microstructure of the

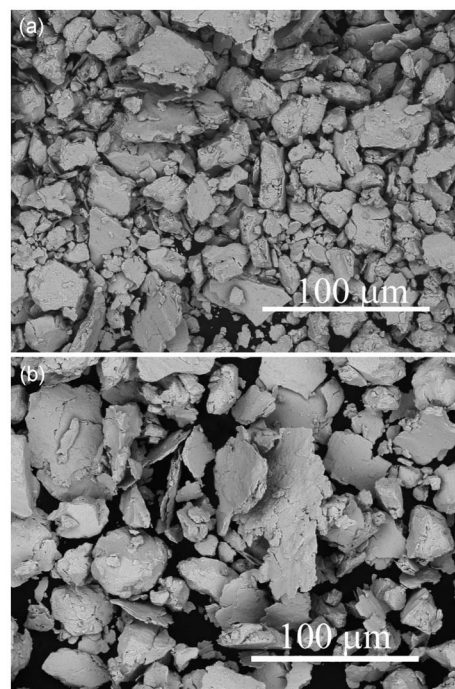
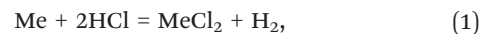


Fig. 1 Morphology of the Ag–Fe (a) and Ag–Ni (b) nanocomposite powders.

agglomerates refines, the grain size of the metals decreasing to the nanolevel. The fine-grained agglomerates become stronger and more brittle, which, in turn, leads to the dominance of fracturing over cold welding and a reduction in their average size. After 60 min of milling, the size of agglomerates ranges from 10 to 80 μm . A relatively narrow size distribution of the composite agglomerates is beneficial for a successful preparation of porous silver by dissolution, as the particles with similar morphology and close dimensions will require approximately the same time for the dissolution of Fe or Ni to be complete. When immersed in HCl solution, iron and nickel start dissolving from the Ag–Fe and Ag–Ni nanocomposites according to the following reaction:



where Me is Fe or Ni.

The XRD patterns of the Ag–Fe and Ag–Ni nanocomposites produced by mechanical milling for 60 min show broadened reflections of Ag, Fe and Ni, while the XRD patterns of the products of phase separation show only Ag reflections confirming the complete dissolution of Fe and Ni and the formation of porous silver (Fig. 2, a–b). The information on the elemental composition of the porous product was also obtained from the EDS spectra taken from the HCl solution-treated agglomerates showing silver as the only remaining component (Fig. S2, ESI†). The XRD reflections of porous silver are narrower than those of Ag in the nanocomposite precursors. The calculations of the size of coherently scattering domains and microstrain of the mechanically milled nanocomposite precursors and porous silver reveal an increase

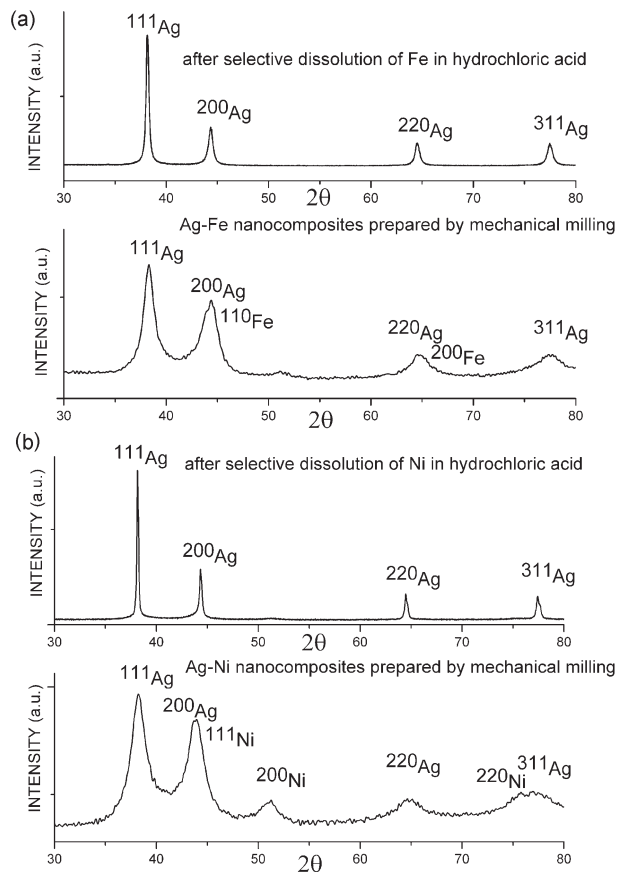


Fig. 2 XRD patterns of the Ag–Fe (a) and Ag–Ni (b) nanocomposite powders and nanoporous silver formed after Fe and Ni have been dissolved.

in the former and a decrease in the latter upon selective dissolution of Fe or Ni (Table 1). A larger size of coherently scattering domains and a reduced microstrain indicate the concurrent processes of porosity generation and recrystallisation in silver during the dissolution.

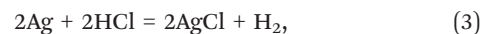
Before starting looking for a plausible explanation of the observed recrystallisation effect, we have analyzed the existing coarsening mechanisms in nanoporous metals. Coarsening of nanocrystalline noble metals immersed in acidic solutions has been observed by several authors;^{7,27–31} the growth of

ligaments of porous Au in concentrated acids is explained by enhanced mobility of surface atoms in the electrolyte environment and curvature-driven diffusion,^{27,28} while the coarsening of Ag nanoparticles and ligaments of a nanoporous structure is assumed to be related to the chemical reactivity of nanocrystalline silver.^{29–31} The dissolution of Ag in HCl solution is thought to occur according to the following reaction:



By observing aggregation of silver nanoparticles in oxygen-free solutions rather than recrystallisation, Pucek *et al.*²⁹ have proved that the presence of oxygen is crucial for the growth of silver nanoparticles. They found an order of magnitude increase in the crystallite size of silver (from 30 nm to 400 nm) within a few minutes of exposure to a concentrated NaCl solution when the experiments were performed in air. Redmond *et al.*³⁰ have shown that the addition of citrate to the solution prevents silver nanoparticles placed on a conductive substrate from growth due to the well-known reducing activity of the citrate ion inhibiting the interaction of silver with air.

Another possibility can also be considered based on the direct reaction of nanostructured silver with hydrochloric acid. Li and Zhu³² argued that silver nanoparticles can react with hydrochloric acid according to the following reaction



which is enabled by a more negative microelectrode potential of silver in its nanocrystalline state. In our case, the silver grains in the nanocomposites produced by mechanical milling bear the characteristic features of metals subjected to severe plastic deformation. The strained state of the lattice after mechanical milling can contribute to an increased reactivity of silver toward hydrochloric acid. In the excess of the acid, the HAgCl_2 complex compound will form in the solution.²⁹ With the formation of a soluble form of silver enabled, the dissolution–precipitation mechanism can operate to result in nanoporous silver with larger crystallites and a more relaxed state of the crystalline lattice.

Table 1 Size of coherently scattering domains and microstrain of the mechanically milled Ag–Fe and Ag–Ni nanocomposites and nanoporous silver produced by phase separation. Note an increased size of coherently scattering domains and a reduced microstrain of the nanoporous silver relative to the mechanically milled Ag–Fe and Ag–Ni nanocomposite precursors

Composition	Size of coherently scattering domains/nm	Microstrain (%)	Size of coherently scattering domains/nm	Microstrain (%)
Ag–Fe mechanically milled	Fe		Ag	
	3.79	0.75	17.05	0.97
Nanoporous Ag by selective dissolution of Fe	Fe		Ag	
	—	—	27.60	0.08
Ag–Ni mechanically milled	Ni		Ag	
	4.53	0.88	10.20	1.43
Nanoporous Ag by selective dissolution of Ni	Ni		Ag	
	—	—	79.53	0.07

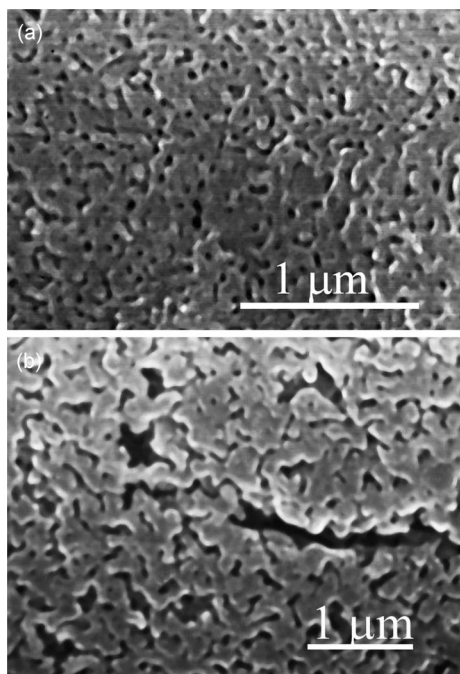


Fig. 3 Microstructure of the nanoporous silver produced by phase separation in the Ag-Fe (a) and Ag-Ni (b) nanocomposites.

The discussed mechanisms are very likely to be valid during the dissolution of the Ag-Fe and Ag-Ni nanocomposites. However, a significant contribution to the recrystallisation process of silver can be also expected from the reactivity of sacrificial Fe or Ni phases. In parallel to experiencing dissolution, these metals can participate in the galvanic displacement reactions:



This reaction, known for decades as a basis for silver recovery from waste,³³ presents yet another path of the recrystallisation process governed by the dissolution-precipitation mechanism.

The porous silver obtained by selective dissolution of the nanocomposite powders features pores ranging from 50 to 200 nm and ligaments approximately in the same size range (Fig. 3, a–b). A relaxed state of the silver lattice relative to that observed in the nanocomposite precursors can lead to a more mechanically robust nanoporous material.²⁸ Once we start seeing silver chloride (AgCl) on the surface of the samples, we can conclude that metallic Fe and Ni have been fully consumed in the reactions and can no longer help in reducing AgCl according to reaction (4). This is the moment the sample should be removed from the HCl solution. Our experiments show that exposure of the nanoporous silver skeleton to hydrochloric acid is not desirable as it leads to Ag losses in the form of AgCl, which forms crystals 10–20 μm in size (Fig. S3, ESI†) after prolonged exposure of the alloys to the solution.

Thermal or mechanical treatments that the starting alloy had experienced before dealloying can be “written” into the microstructure of the porous material and used to advantage. The property enhancement of nanoporous gold—large possible charge-induced strain—achieved owing to a two-length-scale structure (stacked nanoporous layers of submicrometer thickness) was observed by Detsi *et al.*⁶ They have used a cold rolled alloy as a starting material to tailor the bulk structure and properties of nanoporous gold. In our work, we use mechanical milling, which is known to be a versatile technique to produce nanocomposite metallic particles of flaky or equiaxed morphology depending on the ratio of shear and impact stresses imposed on the powders. Advanced milling equipment is currently available to manufacture powder products under controlled mechanical action. There is an intriguing possibility that mechanically milled nanocomposites of tailored microstructure, geometrical distribution of phases and agglomerate morphology and size can possess new interesting properties. This presents a lot of room for further research in the area of nanoporous materials produced by phase separation in a wide range of metallic systems.

Having prepared nanoporous silver through phase separation in a powder state, we directed our efforts to making a bulk porous body. Consolidation and sintering of agglomerated powders into dense compacts are known to present serious challenges. Particles forming agglomerates do not have as much flexibility of rearrangement during compaction as non-agglomerated particles. When agglomerates are nevertheless to be sintered, special measures are required to eliminate inter- and intra-agglomerate porosity. The agglomerates of mechanically milled Ag-Fe and Ag-Ni alloys produced in this work are dense, so it is only the inter-agglomerate pores that need to be removed. Although the nanocomposite agglomerates tend to more easily deform under an applied pressure at elevated temperatures during the sintering process, we can expect very few microstructure changes in the interior regions of the Ag-Fe and Ag-Ni agglomerates as the duration of temperature exposure during the chosen SPS cycle was very short. However, a feature typical of pulsed current sintering and of SPS in particular is a local temperature rise at the inter-particle contacts during the passage of current.³⁴ In the case of sintering of powder agglomerates, it is this SPS feature that can solve the problem of inter-agglomerate pores and ensure more efficient bonding between the particles. As can be seen from a characteristic microstructure of the Ag-Fe SPS-ed compact shown in Fig. 4, a, higher local temperatures caused melting of silver and slight redistribution of phases indicated by the presence of silver streaks in the cross-sectional view of the SPS-ed compact, the distances between which are comparable with the size of the powder agglomerates used for sintering. The presence of these silver layers will exhibit only a minor influence on the bulk nanoporous structure produced from the SPS-ed compact by phase separation as the volume fraction of silver experiencing melting and solidification is limited to a few percent as was estimated from the SEM images. Selective dissolution of Fe from the SPS-ed compact

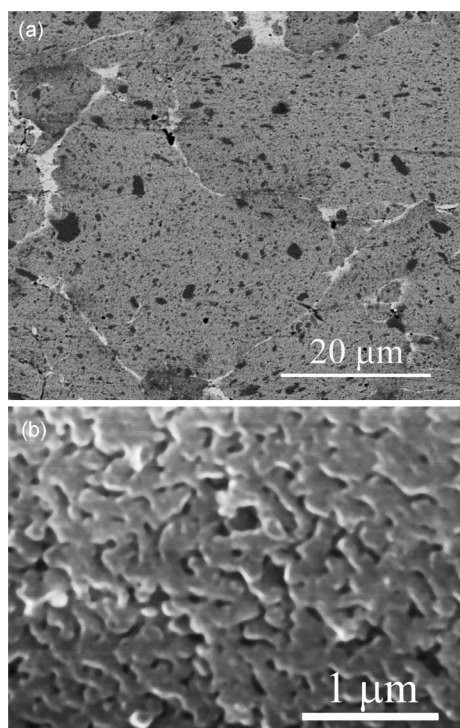


Fig. 4 Cross-sectional view of the SPS-ed Ag-Fe compact (a) and nanoporous silver obtained through phase separation in the SPS-ed compact by selective dissolution of Fe in HCl solution (b).

resulted in the formation of nanoporous silver with pore and ligament sizes ranging from 100 to 200 nm (Fig. 4, b). The importance of using SPS rather than conventional sintering is clearly demonstrated by the microstructure of the Ag-Fe composites annealed in hydrogen at 600 °C (Fig. S4, ESI†). The redistribution of phases and silver coalescence and growth into crystals several microns in size are unavoidable in conventional heat treatment processes.

When single-phase Ag nanopowders are SPS-ed, it is very challenging to keep their grain size unaltered.³⁵ SPS at 300 °C for 5 min gives a compact 98% dense but this successful densification is accompanied by grain growth of Ag from 70 nm in the powder up to 300 nm in the bulk. After the SPS at 600 °C, even larger grains are observed (up to 700 nm). With a higher-melting temperature metal present in the nanocomposites and immiscible with silver, the grain growth of silver is hindered. Indeed, after the SPS at 600 °C, we obtained a material maintaining a nanocomposite structure and giving nanoporous silver after excavation of iron.

Conclusions

In conclusion, we proposed a novel and simple preparation route of nanoporous silver based on selective dissolution of Fe or Ni from Ag-Fe and Ag-Ni nanocomposites. Ag-Fe and Ag-Ni systems are immiscible in both liquid and solid states. We use a convenient way of producing a nanocomposite structure in

these alloys by high-energy mechanical milling of the elemental powders. Upon treatment of the Ag-Fe and Ag-Ni nanocomposite powders containing 50 vol.% Ag in diluted HCl solution, Fe and Ni are dissolved to leave behind a nanoporous silver skeleton. The size of coherently scattering domains of the nanoporous silver is somewhat larger than that of the starting nanocomposite before the phase separation, while the microstrain is reduced. We suggest that the phase separation process is accompanied by partial recrystallisation of silver occurring through the dissolution-precipitation mechanism. This mechanism is enabled by oxidation of silver by oxygen of ambient air and the formation of HAgCl₂ in the solution followed by its reduction by metallic Fe or Ni in a galvanic displacement reaction. Our findings show that when phase separation by selective dissolution is used for making porous materials, it is important to take into account possible chemical reactions, in which the sacrificial phases can be involved. This study suggests a new mechanism of microstructure tailoring of nanoporous silver produced by phase separation. The dual functionality of Fe and Ni—as sacrificial phases and reducing agents—during the interaction of Ag-Fe and Ag-Ni nanocomposites with hydrochloric acid is a key advantage of the selected metallic pairs. The reducing action of Fe and Ni prevents the losses of silver in the form of AgCl, which is the product of reaction of nanocrystalline silver with hydrochloric acid. The significance of the developed technique is in its versatility; other pairs of immiscible metals can be chosen provided that their chemical and electrochemical properties will differ in such a way that microstructure tuning possibilities described here are possible. As an expansion of our research, we consolidated the Ag-Fe and Ag-Ni alloys by Spark Plasma Sintering into compacts retaining silver nanograins and showing only limited phase redistribution caused by melting. The selective dissolution performed on these compacts can be used to produce porous silver bodies of selected geometry. From the application viewpoint, this offers a convenient method of making nanoporous silver membranes.

Acknowledgements

The authors are grateful to Dr Vyacheslav I. Mali and Dr Alexander G. Anisimov (Lavrentiev Institute of Hydrodynamics, Siberian Branch of the Russian Academy of Sciences, Novosibirsk) for their help with Spark Plasma Sintering experiments and Ms. Nelly A. Tukalo (Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk) for the assistance in conducting mechanical milling operations.

References

- 1 J. Erlebacher, M. J. Aziz, A. Karma, N. Dimitrov and K. Sieradzki, *Nature*, 2001, **410**, 450.

- 2 D. Mukherji, G. Pigozzi, F. Schmitz, O. Näth, J. Rösler and G. Kistorz, *Nanotechnology*, 2005, **16**, 2176.
- 3 J. Weissmüller, R. C. Newman, H. J. Jin, A. M. Hodge and J. W. Kysar, *MRS Bull.*, 2009, **34**, 577.
- 4 Y. Ding and M. Chen, *MRS Bull.*, 2009, **34**, 569.
- 5 H.-J. Jin, X.-L. Wang, S. Parida, K. Wang, M. Seo and J. Weissmüller, *Nano Lett.*, 2010, **10**, 187.
- 6 E. Detsi, S. Punzhin, J. Rao, P. R. Onck and J. Th. M. De Hosson, *ACS Nano*, 2012, **6**, 3734.
- 7 N. A. Luechinger, S. G. Walt and W. J. Stark, *Chem. Mater.*, 2010, **22**, 4980.
- 8 X. F. Zhang, G. Harley and L. C. De Jinghe, *Nano Lett.*, 2005, **5**, 1035–37.
- 9 E. Ma, *Prog. Mater. Sci.*, 2005, **50**, 413.
- 10 T. Bregel, W. Krauss-Vogt, R. Michal and K. E. Saeger, *IEEE Trans. Compon., Hybrids, Manuf. Technol.*, 1992, **14**, 8.
- 11 N. A. Luechinger, R. N. Grass, E. K. Athanassiou and W. J. Stark, *Chem. Mater.*, 2010, **22**, 155.
- 12 C. Suryanarayana and N. Al-Aqeeli, *Prog. Mater. Sci.*, 2013, **58**, 383.
- 13 P. H. Shingu, K. N. Ishihara and A. Otsuki, *Mater. Sci. Forum*, 1995, **179–181**, 5.
- 14 H. Qiu, Z. Zhang, X. Huang and Y. Qu, *ChemPhysChem*, 2011, **12**, 2118.
- 15 H. Jing, Z. Yu and L. J. Li, *Biomed. Mater. Res.*, 2007, **87A**, 33.
- 16 H. Ji, X. Wang, C. Zhao, C. Zhang, J. Xu and Z. Zhang, *CrystEngComm*, 2011, **13**, 2617.
- 17 E. Detsi, Z. Vuković, S. Punzhin, P. M. Bronsveld, P. R. Onck and J. Th. De Hosson, *CrystEngComm*, 2012, **14**, 5402.
- 18 C. L. Wang, S. Z. Lin, Y. Niu, W. T. Wu and Z. L. Zhao, *Appl. Phys. A: Mater. Sci. Process.*, 2003, **76**, 157.
- 19 J. Xu, U. Herr, T. Klassen and R. S. Averback, *J. Appl. Phys.*, 1996, **79**, 3935.
- 20 N. Kataoka, K. Sumiyama and Y. Nakamura, *J. Phys. F: Met. Phys.*, 1988, **18**, 1049.
- 21 J. Kuyama, H. Inui, S. Imaoka, S. Nasu, K. N. Ishihara and P. Shingu, *Jpn. J. Appl. Phys.*, 1991, **30**, L854.
- 22 G. Rexicker, *Solid State Commun.*, 2002, **122**, 299.
- 23 T. Spassov, L. Lyubenova, Y. Liu, S. Bliznakov, M. Spassova and N. Dimitrov, *J. Alloys Compd.*, 2009, **478**, 232.
- 24 Z. A. Munir, D. Quach and M. Ohyanagi, *J. Am. Ceram. Soc.*, 2011, **94**, 1.
- 25 J.-S. Kim, Y.-S. Kwon, O. I. Lomovsky, M. A. Korchagin, V. I. Mali and D. V. Dudina, *Mater. Lett.*, 2006, **60**, 372.
- 26 W. Kraus and G. Nolze, *PowderCell for Windows, V2.4*, Federal Institute for Materials Research and Testing, Berlin, Germany, 2000.
- 27 M. Hakamada and M. Mabuchi, *Nano Lett.*, 2006, **6**, 882.
- 28 S. Van Petegem, S. Brandstetter, R. Maass, A. M. Hodge, B. S. El-Dasher, J. Biener, B. Schmitt, C. Borca and H. Van Swygenhoven, *Nano Lett.*, 2009, **9**, 1158.
- 29 R. Prucek, A. Panáček, A. Fargašová, V. Ranc, V. Mašek, L. Kvitek and R. Zbořil, *CrystEngComm*, 2011, **13**, 2242.
- 30 P. L. Redmond, A. J. Hallock and L. E. Brus, *Nano Lett.*, 2005, **5**, 131.
- 31 B. Wiley, T. Herricks, Y. Sun and Y. Xia, *Nano Lett.*, 2004, **4**, 1733.
- 32 L. Li and Y.-J. Zhu, *J. Colloid Interface Sci.*, 2006, **303**, 415.
- 33 J. A. Murphy, A. H. Ackerman and J. K. Heeren, *J. Chem. Educ.*, 1991, **68**, 602.
- 34 X. Song, X. Liu and J. Zhang, *J. Am. Ceram. Soc.*, 2006, **89**, 494.
- 35 Y. Q. Fu, C. Shearwood, B. Xu, L. G. Yu and K. A. Khor, *Nanotechnology*, 2010, **21**, 115707.