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Fractal structures of highly-porous metals and alloys at the nanoscale

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ABSTRACT

The fabrication of nanoporous alloys with uniform compositions has been a synthetic challenge in the last two decades. Fine nanoscale porosity in metals is usually obtained by destructive dealloying of bulk cast alloys, whereas nanoscale bimetallic alloys have been prepared by a rather sophisticated method, namely, the reduction of bimetallic ionic complexes. However, the physical properties of these alloys have not been fully elucidated and the generality of the methods remains limited. We show that chemical reduction of metal complexes at a low but constant temperature preserves alloy composition and produces a highly-porous metallic material (>90% porosity) with open interconnected fractal porosity extended down to a nanoscale. These porous metallic materials that consist of nanocrystallites can be obtained for a wide range of binary systems and pure metals (binary systems: Pt_3Ru_2, Co_2Pt_3, CoPt, Co_2Pt, IrPt, Rh_2Ru, Rh_3Ru_2, RhRu, Ir_2Ru, IrRu; pure metals: Co, Ru, Rh, Pd, Ag, Ir, Pt). Geometrical analysis of several nanoporous metals and alloys suggests that the three-dimensional structure of these materials may be represented by a mathematical fractal model.

1. Introduction

Nanocrystals of metallic materials such as pure metals or alloys exhibit unusual mechanical [1–11], magnetic [12–14], electrical [15–17], and optical [18–21], properties as compared to their bulk counterparts. Metallic materials with nanoscale porosity are of critical importance in catalysis, sensing, adsorption and other technologies [22–25]. However, due to fundamental limitations in preparation processes, advanced synthetic techniques leading to nanoporous metallic materials are yet to be developed. Conventional metallurgical methods based on melting-solidification or deformation techniques are not applicable in preparation processes of nanoporous nanostructured metallic materials [26,27]. Still, nanoscale porosity can be achieved through *destructive* techniques such as dealloying [28,29] or galvanic displacement [30–32]. Such techniques, however, do not produce composition uniformity, do not allow control of elemental composition within the end products and produce porosity only in a limited volume [33–41]. Chemical processes in which metal complexes of the individual alloyed metals are mixed in solution and co-reduced to get alloyed nanoparticles are also known [42,43]. However, this method does not allow any control over the final composition and uniformity of the resulting alloys. A more sophisticated synthetic approach utilizes molecular [44] or ionic precursors [45,46] that contain the alloyed elements in a precise atomic ratio. Thermolysis or chemical reduction of such precursors may produce powdered metallic materials with nanoscale crystallite size in which the elemental ratio is preserved. Recently, Shubin *et al.* reported that thermal decomposition of $[Pd(NH_3)_4][AuCl_4]_2$ led to the formation of $PdAu_2$ nanoporous structure [46]. However, direct measurements of pore sizes are not reported and it seems that nanoporosity in this system has been deduced primarily from EM images. Furthermore, the authors did not perform an in-depth study of this porosity and did not explain its origin. In addition, nanoporosity was demonstrated only for a particular Au–Pd alloy composition but not for other compositions or metallic materials.

In the present work we show that chemical reduction of metal complexes by hydrogen, at a low but constant temperature, not only preserves alloy composition but also produces a highly porous metallic material (>90% porosity) with open interconnected *fractal* porosity extended down to the nanoscale, namely, a highly-porous fractal metallic material (HPFMM). These porous metallic materials that consist of nanocrystallites can be obtained for a wide range of binary systems and pure metals.

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2. Experimental

2.1. Sample preparation

2.1.1. Bicomplex salt (BCS) preparation

In a typical procedure, a concentrated aqueous solution of the chloride salt of a cationic complex containing one metallic ion was prepared. Another concentrated aqueous solution of the ammonium, sodium or potassium salt of an anionic complex containing another metallic ion was also prepared. Tens of milligrams of the above mentioned salts were weighed and dissolved in equal volumes of deionized water. Stoichiometric ratios between the two complex-ion solutions were achieved by weighing the salts. The two solutions were poured into one another. An immediate microcrystalline precipitate was obtained. The precipitate was separated, washed three times with deionized water and one time with acetone and left to dry in an open vessel. The resulting dry bicomplex salt was characterized using PXRD, HR–SEM, and HR–SEM–EDS techniques.

When feasible, single crystals of the BCSs were prepared using membrane diffusion techniques.

2.1.2. Pure metal and alloy preparation

In a typical procedure, tens of milligrams of a bicomplex salt were flattened on the surface of an alumina-made boat and the boat was slid into a quartz-tube furnace. 95%/5% mixtures of N_2/H_2 or Ar/H_2 (where the former is the carrier gas and the latter is the reducing agent) were passed over the salt. After the tube was filled with gas, heating was introduced. The salt was heated to a final constant temperature within the range of 150–550 °C, depending on the reaction specifics. Within minutes up to hours from the beginning of heating, the salt changed its color to black or silvery black. Total reaction times were 24 h to 72 h. The resulting metallic powders were characterized using PXRD, HR–SEM, HR–SEM–EDS, HR–TEM, HR–TEM–ED, STEM, STEM–EDS, and ICP–MS techniques.

HPFMMs and their corresponding salt precursors are detailed in Table S1.

2.2. Instrument specifications

2.2.1. Single-crystal X-ray diffraction (SC-XRD) analysis

In a typical analysis, a BCS single crystal was transferred to a Bruker SMART APEX CCD X-ray diffractometer equipped with a graphite monochromator. The system was controlled by a pentium-based PC running the SMART software package [51]. Data were collected at 295 or 298 K using Mo Kα radiation ($\lambda = 0.71073$ Å). Immediately after collection, the raw data frames were transferred to a second PC computer for integration and reduction by the SAINT program package [52]. The structure was solved and refined by the SHELXTL software package [53].

[CCDC 995882 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif].

[Further details of the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-427575, 427576, 427577, 427578, 427579].

2.2.2. Powder X-ray diffraction (PXRD) analysis

Powder X-ray diffraction patterns were measured using a Philips PW1820 diffractometer with a Philips PW1710 proportional detector. The software package, Philips PW1877/43 PC-APD version 3.5, was used for diffractometer control, data collection and data processing. The powder diffractometer is equipped with a Cu sealed tube and a graphite monochromator providing Cu Kα radiation (Kα1 $\lambda = 1.54060$ Å, Kα2 $\lambda = 1.54439$ Å). The Cu tube operating conditions: voltage of 40 kV and current of 30 mA. XRD measurements were recorded in Bragg–Brentano reflection geometry. The scan was performed in the 2θ ranges of 10–60° for salts and 30–90° for metallic materials, with a step width of 0.02° and a step time of 1 s.

2.2.3. Electron microscopy

i. HR–SEM & XHR–SEM: High-resolution scanning electron microscopy measurements were performed using an FEI Sirion HR–SEM equipped with EDAX EDS and Magellan 400L XHR–SEM equipped with an Oxford Instruments XMAX SDD EDS working on an INCA450 platform.
ii. HR–TEM: High-resolution transmission electron microscopy measurements were performed using an FEI Tecnai F20 G2 (S) HR–TEM equipped with EDAX EDS.

3. Results and discussion

Pure Co, Ru, Rh, Pd, Ag, Ir, and Pt and some of their binary alloys were prepared by low-temperature reduction of crystalline salts of metal complexes containing one or two different metal atoms per formula unit. A typical reduction has been performed by using a mixture of 5% hydrogen in nitrogen or argon (a carrier medium) at 150–550 °C. Detailed reactions are described in the Supplementary Information, part 1. A general reaction for a bimetallic system is described in Eq. (1):

$$[M^1L^1_m]_x[M^2L^2_n]_y \xrightarrow[150-550\,^\circ C]{H_2} M^1_xM^2_y + \text{volatile products} \qquad (1)$$

M^1, M^2 and L^1, L^2 represent metal atoms and a set of ligands, respectively. The stoichiometric ratio x:y is preserved during the reduction process in which the system is transformed from a salt to an alloy. The formation of a pure metal can be achieved by using either the precursor in Eq. (1) in which $M^1 = M^2$ or a single metal complex.

In order to demonstrate the entire experimental process of transforming a metal complex salt into an alloy (Eq. (1)) and the full physical characterization of both the precursor and the metallic material, we have chosen a binary system, namely, Rh_2Ru. The crystalline binary compound $[Rh(NH_3)_5Cl]_2[Ru(CN)_6]\cdot 4H_2O$ (**1**) was prepared and structurally characterized by single-crystal X-ray diffraction (Supplementary Information, part 2). A powdered sample of **1** was reduced under a stream of 5% hydrogen in nitrogen at 300 °C for 48 h. Fig. 1 shows structural details of precursor **1** (left panel) and the obtained alloy Rh_2Ru (right panel).

The unit cell of **1** along with the overlaid simulated and experimental powder XRD patterns are shown in Fig. 1a. The perfect match between the two patterns indicates the purity of the microcrystalline sample of **1**. Hence, the Rh:Ru ratio is unambiguously pre-defined prior to the reduction process. HR–SEM imaging of a powdered sample of **1** (Fig. 1b) reveals smooth-faced rectangular prisms with micrometer-scale dimensions. An average elemental ratio Rh/Ru of 1.9 has been measured by energy-dispersive X-ray spectroscopy (EDS) in SEM on a microcrystalline sample of **1** (EDS spectrum in the Supplementary Information, part 3, Fig. S1). This result is in very good agreement with the stoichiometric ratio between rhodium and ruthenium in **1** as determined by X-ray crystallography. Powder XRD analysis of the reduction product indicated the presence of two crystalline phases: a Rh-based solid solution with a face-centered cubic (f.c.c.) lattice and a Ru-based solid solution with a hexagonal (h.c.p.) lattice (Fig. 1c). The composition of the alloy has also been determined by an EDS measurement (Supplementary Information, part 3, Fig. S2) yielding an average Rh:Ru ratio of 1.9. We conclude that the reduction product is indeed a binary alloy with a pre-defined Rh:Ru ratio of 2.0 having a two-phase crystalline structure. The crystallite domain size of the alloy has been calculated by the Scherrer formula and found to be nanometric (7–10 nm). As shown in Fig. 1d, each Rh_2Ru particle consists of interconnected nanocrystallites and possesses a very specific morphology. On the one hand, the alloy particles are morphologically identical to the crystals of the BCS precursor of **1** (Fig. 1b) and have almost the same volume. On the other hand, the particles are extremely porous as can be clearly observed in the HR–SEM images in Figs. 1 and 2, and HR–TEM images in Fig. 3. Porosity of the alloy constituents, pure Rh and pure Ru, is also shown in Fig. 2 HR–SEM images.

During the reduction of **1** all ligands and solvent molecules, that constitute about 60% of the precursor's mass, are removed from the system as volatiles leaving only metallic material behind. Since the volume of the resulting particle preserves the original dimensions of the precursor crystal, the dramatic increase in the density of the system from 1.912 to 12.3 g cm^{-3} explains the formation of a sponge-like, highly-porous 3D alloy. Porosity is calculated by using Eq. (2):

$$\text{Por} = 100 \times \left(1 - \frac{\rho_S \cdot f_M}{\rho_M}\right) \qquad (2)$$