Materials Science and Engineering B 177 (2012) 27–33

Contents lists available at SciVerse ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Structural and magnetic properties of Ni–Pt nanoalloys supported on silica

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ARTICLE INFO

Article history:
Received 5 May 2011
Received in revised form 31 July 2011
Accepted 4 September 2011
Available online 20 September 2011

Keywords:
Nanoparticles
Ni_3Pt
$NiPt_3$
NiSi
Radiolysis
Magnetization

ABSTRACT

Bimetallic Ni–x%Pt/SiO_2 nanoclusters at different initial platinum contents ($x = 0$, 2, 9, 15, 25, 35, 85 and 95 at %) are synthesized at room temperature by the radiolytic process. According to the Pt amount, the structural studies (XRD, TEM and SAED) reveal the presence after irradiation of NiSi and Ni_3Pt or $NiPt_3$ nanoalloyed clusters on amorphous silica. The Ni–Pt nanoparticles have a fcc solid solution structure and a narrow cluster size distribution. The radiation-induced nanoparticles exhibit an enhancement of the magnetization at low temperature. Moreover, unlike Ni–Pt bulk alloys, the magnetization increases with the Pt content. In the ultra divided state, platinum seems to play a major role by enhancing the nickel ion reduction and protecting Ni against corrosion during the synthesis.

1. Introduction

For some years now, the ability to synthesize nanoscaled objects constitutes a challenge for most of laboratories in material sciences. The study of these materials has a great impact in nanoscience and nanotechnology. In this mesoscopic state, which is intermediate between isolated molecules and condensed matter, the material dimension is in the same range as the characteristic sizes of the physical properties. The clusters exhibit original structures and size-dependent physical and chemical properties [1–6]. Concerning magnetic properties, some materials such as palladium or rhodium, which are known to be not ferromagnetic in the bulk state, exhibit new magnetic properties at nanometric sizes [7–9]. An enhancement of the local orbital moment is revealed by experimental investigation [10] and self-consistent calculations [11,12]. In fact, in the ultra-divided state, the size of ferromagnetic aggregates approaches the length scale of the magnetic domains. Therefore, there is a critical size for which they become homogeneous monodomains. Thus, they acquire a superparamagnetic behavior obeying the Langevin law [13,14]. The single domain particles can be viewed as a giant classical magnetic moment (Stoner–Wohlfart particles). Their magnetic behavior is governed by lattice and shape anisotropies. The study of the magnetic behavior of nano-sized materials improves our fundamental knowledge of magnetism. It becomes free from the complexity due to the interfaces and allows a better understanding of the progressive changes of magnetism from the macroscopic to nanoscopic state of matter [15].

Among magnetic materials, nickel is widely used in technological and biological systems for magnetic recording or as ferrofluids for medical imaging. The nickel clusters found unique applications in the field of nanotechnology, namely spintronics, nanomagnetism [13–16], nanosynthesis (carbon nanowires growth) [17] and catalysis [18–23]. Bimetallic clusters formed with 3d and 4d or 5d elements such as Co–Pd or Ni–Pt systems are specially interesting because of the strong magnetic susceptibility of 4d (5d) elements and of the high magneto-anisotropy of the 3d–4d (5d) interfaces [6,24,25]. When the clusters are deposited, the interaction of the magnets with the substrate plays a major role [26–32]. It is admitted that these properties are highly dependent on the preparation conditions [29–31]. A correlation between the chemical and the magnetic order is established [33,34].

Silica is largely used as nanoparticle support, particularly in catalysis. In recent years, magnetic nanocomposites dispersed in silica matrix have taken much attention of researchers because of their specific magnetic properties, different from that of their equivalent pure or bulk materials [35–37].

In previous studies, it has been proved that radiolysis is a potent method to obtain highly dispersed, size-controlled and homogeneously size-distributed metal clusters [2,3,38,39]. They display specific properties depending on the irradiation conditions. However, in contrast with the abundance in the literature of studies on the various properties of the radiation-induced clusters, their magnetism has been rarely considered. The radiation-induced reduction of a solution containing two different types of free ions

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doi:10.1016/j.mseb.2011.09.025

may result into segregated phases or ordered alloys favored at high dose rate [3]. It has been demonstrated that the kinetical aspect is predominant compared to the thermodynamical one. The reduction of both types of ions is in competition with the slow intermetal electron transfer reactions from the less noble metal atoms to the other metal ions. Therefore, at low dose rate, the process results in a core-shell structure whereas at high dose rate an alloy is obtained [3,38]. In the present work, the challenge is to study the magnetism of nickel clusters in spite of their well-known extreme fragility to oxidation. Alloying of nickel with platinum is indeed helpful for their stabilization. Therefore, silica-supported small Ni–Pt/SiO_2 nanoclusters at various initial platinum contents are synthesized using radiation-induced reduction of nickel and platinum complexes, which are previously anchored on SiO_2. The structural properties and the magnetic behavior of the synthesized samples are examined. Since very small clusters with narrow size-distribution can be generated using the radiolytic process, it is expected to induce the formation of magnetic mono-domain particles. The major aim is to use the specificity of the radiolysis in order to explore new magnetic properties for potential applications.

2. Principle of the radiolytic synthesis

2.1. Radiolytic species

The radiolytic process consists in reducing the metal ions to the zerovalent state of the metal by irradiating the system using ionizing radiation [1–3,38–40]. The interaction of ionizing radiation with a solution of metal ions induces excitation and ionization of the solvent in the earlier steps, followed by the reactions between the primary species produced. For example, it can be summarized in the case of aqueous solution by:

$$H_2O \rightarrow H_2O^*, H_2O^+, e^- \rightarrow e_{aq}{}^-, H_3O^+, H^\bullet, OH^\bullet, H_2, H_2O_2 \quad (1)$$

The reducing species, mainly solvated electrons ($e_{aq}{}^-$), achieve the metal ion reduction to lower valencies and finally to metal atoms. In order to avoid reverse oxidation reactions by $OH^\bullet$ radicals, a specific scavenger is added (an alcohol or formate ions). This latter reacts also with H atoms. Secondary radicals ($(CH_3)_2{}^\bullet COH$ or $CO_2{}^{-\bullet}$) are formed which behave also as strong reducing agents.

$$OH^\bullet + ((CH_3)_2CHOH \text{ or } HCO_2{}^-) \rightarrow H_2O + ((CH_3)_2{}^\bullet COH \text{ or } CO_2{}^{-\bullet}) \quad (2)$$

$$H^\bullet + ((CH_3)_2CHOH \text{ or } HCO_2{}^-) \rightarrow H_2 + ((CH_3)_2{}^\bullet COH \text{ or } CO_2{}^{-\bullet}) \quad (3)$$

2.2. Metal ion reduction

The radiolytic reduction of multivalent metal ions, such as Ni^{2+} or $Pt^{II}Cl_4{}^{2-}$, is a multi-step process which has been already described [3]. *Via* this method, isolated nascent metal atoms are first formed.

Metal ions are efficiently reduced by $e_{aq}{}^-$ and $(CH_3)_2{}^\bullet COH$ or $CO_2{}^{-\bullet}$ to monovalent ions then atoms. The overall reactions are as follows:

$$Ni^{2+} + 2e_{aq}{}^- \rightarrow Ni^0 \quad (4)$$

$$Ni^{2+} + 2((CH_3)_2{}^\bullet COH \text{ or } CO_2{}^{-\bullet}) \rightarrow Ni^0 + 2((CH_3)_2CO + H^+ \text{ or } CO_2) \quad (5)$$

$$Pt^{II}Cl_4{}^{2-} + 2e_{aq}{}^- \rightarrow Pt^0 \quad (6)$$

$$Pt^{II}Cl_4{}^{2-} + 2((CH_3)_2{}^\bullet COH \text{ or } CO_2{}^{-\bullet}) \rightarrow Pt^0 + 2Cl^- + 2((CH_3)_2CO + H^+ \text{ or } CO_2) \quad (7)$$

The Ni^0 or Pt^0 atoms then coalesce into oligomers and clusters. However, because of their binding to the support surface, the mutual diffusion of atoms is strongly hindered, particularly at room temperature. Finally, the metal aggregates obtained are very small. Alloyed Ni–Pt nanocolloids are found when a mixed solution of Ni^{2+} and $Pt^{II}Cl_4{}^{2-}$ is irradiated [2]. The dose rate-dependence of the homogeneous nucleation in solution of core-shell or alloyed clusters was studied, by steady or pulse irradiation techniques [3]. However, few data were collected on the mechanism of the reduction and formation processes of mono- or multi-metallic clusters generated by radiolysis at the surface of supports [18,20].

Note that the radiolytic process is currently employed, using "Electron beam" irradiation, for mass production of polymers or for the depollution of waste waters, etc. It can certainly be used for practical catalyst or magnetic materials mass production.

3. Experimental

3.1. Chemical reagents

The solvent was water of ultra-high purity, obtained with α-Q Millipore apparatus. The resistivity was 18 MΩ cm. The chemicals were supplied with the highest purity available and used as such from Prolabo for NH_4COOH (0.1 M), or from Merck for $Ni(HCOO)_2 \cdot 7H_2O$ and from Strem for $[Pt(NH_3)_4]^{2+}$, $2Cl^-$. The support was silica Aerosil 200 m^2/g from Degussa.

3.2. Sample preparation

The samples were first prepared through impregnation by ionic exchange. The support (SiO_2) particles were immersed into the solutions of nickel formate $Ni(HCOO)_2$ and $[Pt(NH_3)_6]^{2+}$, $2Cl^-$ at variable concentrations corresponding to the loading. The initial concentration of Ni^{2+} was 1.5×10^{-2} mol l^{-1} (880 mg l^{-1}) and the amount of SiO_2 was 17.6 g l^{-1}. This corresponds to a nickel loading on SiO_2 of 3 wt% (1.5 ml of solution *per* 140 mg of SiO_2). The initial concentration of Pt^{II} was changed from 0 to 10^{-2} mol l^{-1}. The volume of samples was generally completed to 10 ml. The pH was adjusted, after adding SiO_2 particles, until obtaining the hexamine complex $[Ni(NH_3)_6]^{2+}$, which was characterized by the 364 nm absorbance. The complex $[Pt(NH_3)_6]^{2+}$ was also formed. As a positively charged ion, it adsorbs better on SiO_2 than the negative chloro-complex. The samples were noted Ni–*x*%Pt, where *x*% is the initial ionic content of platinum. Note that the metal is highly dispersed on silica and therefore very low quantities of Pt are needed.

After the impregnation step, the samples were deaerated by nitrogen bubbling. Then, they were irradiated by γ-rays of ^{60}Co (2500 Curies panoramic source in Laboratoire de Chimie Physique, dose rate 10 kGy h^{-1}). Because the reduction yield of Ni^{2+} is known to be low and the superficial concentration is rather high, the dose of 250 kGy was applied in order to reduce all the ions.

It is worthy to note that the nickel atoms, exhibiting a very negative reduction potential, are known to be easily oxidized by the medium and re-oxidized into Ni^{2+} [40]. Actually, the efficiency of the reduction is therefore much lower for Ni than expected from the yield of radiolytic species. In contrast, platinum ions may be considered reasonably as totally reduced. When nickel is associated with an increasing ratio of platinum atoms, the reduction potential is less negative and the nickel atoms are stabilized. Because the real values of the nickel yield are unknown, all values of the metal content given in the rest of the text and in figures concern the initial relative content of ionic precursors.

After reduction, the solution is transparent. Before characterization and magnetic measurements the samples were dried using