Journal of Physics and Chemistry of Solids

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Manuscript Number:			
Article Type:	Full Length Article		
Keywords:	Pd nanoalloys, ferromagnetic noble metal nanoalloys, liquid-assisted mechanochemical synthesis		
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Abstract:	In this work, we present and discuss the magnetic properties of relatively low silver content Pd100-xAgx nanoalloys (x = 0, 2, 5, 10) obtained by a low cost solvent-assisted mechanochemical synthetic route. Formation of Pd-Ag solid solutions was verified by X-ray diffraction and electron microscopy analyses. Room temperature magnetic characterization of these nanoalloys indicated a paramagnetic response characterized by a magnetic moment lying within the range 0.92 – 1.95 Bohr magnetons. In contrast, magnetization curves at 5 K exhibited ferromagnetic behavior together with coercive fields between 20 -168 Oe. The influence of Ag on the electronic structure of the Pd100-xAgx nanoalloys was characterized by X-ray Photoelectron Spectroscopy analysis, for which a charge transfer mechanism determines the magnetic response observed for the nanoalloys studied.		
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Magnetic Properties of Pd-Ag Nanoalloys Obtained by Mechanochemical Synthesis

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Highligths

Magnetic properties of Pd-Ag nanoalloys are presented and discussed. Interestingly, none of both metals are magnetic in its bulk form.

Mechanochemical synthetic route was shown as an effective and low-cost method for obtaining Pd-Ag nanoalloys

The effect of the incorporation of Ag atoms on the magnetic response of Pd-Ag nanoalloys was correlated with a charge transfer mechanism evidenced by XPS characterization.

Additional functionalities of Pd-based nanoalloys were demonstrated besides to their well known catalytic activity.

Abstract

In this work, we present and discuss the magnetic properties of relatively low silver content $Pd_{100-x}Ag_x$ nanoalloys (x = 0, 2, 5, 10) obtained by a low cost solvent-assisted mechanochemical synthetic route. Formation of Pd-Ag solid solutions was verified by X-ray diffraction and electron microscopy analyses. Room temperature magnetic characterization of these nanoalloys indicated a paramagnetic response characterized by a magnetic moment lying within the range 0.92 - 1.95 Bohr magnetons. In contrast, magnetization curves at 5 K exhibited ferromagnetic behavior together with coercive fields between 20 -168 Oe. The influence of Ag on the electronic structure of the $Pd_{100-x}Ag_x$ nanoalloys was characterized by X-ray Photoelectron Spectroscopy analysis, for which a charge transfer mechanism determines the magnetic response observed for the nanoalloys studied.

Keywords: Pd nanoalloys, ferromagnetic noble metal nanoalloys, liquid-assisted mechanochemical synthesis

1.INTRODUCTION

Nanoparticles of the so-called platinum group elements: Ru, Rh, Pd, and the heaviest, Ir, Os and Pt, as well as the combination between them and with other metals, have been widely studied, mainly due to their catalytic properties [1-5]. Nevertheless, the magnetic response of these metallic elements, especially for 4d elements: Ru, Rh and Pd, is an interesting topic because of the possibility to develop magnetic behavior at room temperature, like their isoelectronic Fe, Co and Ni. For these elements, their spontaneous magnetization can be explained in terms of the displacement between the spin-up and spin-down bands at the Fermi level. A useful parameter to verify this condition is the Stoner criterion, for which the expression $U \cdot g(E_F) \ge 1$ yields to magnetic behavior (*U* represents Coulomb energy and $g(E_f)$ is the density of states per atom at Fermi level). [6]. (Fig. S1). For bulk Ru and Rh metals, the product $U \cdot g(E_F)$ is closer to 1 (compared with other metals in its neighborhood, like Ru, Rh and Ag), and hence, Pd is at the verge for exhibiting ferromagnetism [6]. The condition $U \cdot g(E_F) \ge 1$ for Pd can be achieved by means of the modulation of $g(E_F)$ throughout confinement effects [8-11], changes in local symmetry, vacancies, extensive grain boundaries or variations of the lattice parameter [10, 12].

In this context, the localization of surface electrons due to capping agents as well as the presence of crystal defects can lead to magnetic behavior in otherwise nonmagnetic materials, particularly, in noble metal nanoparticles [13, 14]. In this sense, Kowlgi and coworkers [14] have reported magnetism in Pt nanoparticles synthesized under external magnetic field; the magnetic response of this Pt nanoparticles. Furthermore, it is also known that incorporating 3d transition metals "impurities" like Fe, Co and Ni into Pd clusters is an effective way to modulate their magnetic response in the resulting bimetallic nanoalloy [15-17]. For example, a superparamagnetic behavior has been reported for Pd-Fe and Pd-Ni nanoparticles [18-22]. On the other hand, theoretical reports based on *ab-initio* calculations for the magnetic properties of bimetallic nanoalloys of 3d-4d transition elements predicts interesting behaviors, such as quenched magnetic moments or electronic charge transfer that changes its sign in a stoichiometry-dependent way [23]. In particular, Reddy and coworkers have theoretically demonstrated that small quantities of 4d metals atoms into Pd clusters produce the same effect that Fe impurity, leading to the resulting bimetallic cluster in a magnetic one [24]. However, the effect of alloying Pd with 4d metal "impurities" has been barely reported.

Concerning the synthetic methodologies for obtaining nanoalloys, it is worth to mention that chemical reduction is a well-known and widely used route, due to its versatility and the capability to control size and shape of nanoparticles by means of concentration of precursors and the presence of surfactants [25]. Among the most common variants of chemical reduction are: polyol [26], microwave-assisted polyol [19 27] and hydrothermal and galvanic displacement (successive reduction method) [28]. However, the chemical reduction can also be achieved in solid state by a solvent-assisted mechanochemical approach, [29] which consists of a grinding process of simple metal precursors (metal nitrates or chlorides), together with a reducing agent and few additional drops of methanol as grinding assistant [30]. This method presents significant advantages like the possibility of being carried out at room temperature conditions by using tiny amounts of solvents, in contrast with other chemical methods [31-35]. Besides, this approach has been already explored by our group for the synthesis of Pd-Ag nanoalloys of barely miscible components, like Ag and Bi [31].

In this work, we present and discuss the structural and magnetic behavior of $Pd_{100-x}Ag_x$ nanoalloys (x= 0, 2, 5 and 10). The alloying of Pd with Ag was selected due to their mutual miscibility, both metals having a fcc lattice with only a 5% of difference in their relative atomic radii and similar electronegativity.

2.MATERIALS AND METHODS

2.1. Synthesis

For the synthesis of the $Pd_{100-x}Ag_x$ nanoalloys we followed a previously reported synthetic methodology [7], which consists in a liquid-assisted mechanochemical reduction of a metals precursors mixture. This work was focused on relatively low silver concentrations $Pd_{100-x}Ag_x$ nanoalloys with x = 0, 2, 5 and 10.As an example, for the synthesis of $Pd_{95}Ag_5$ we require 96.16 mg of palladium chloride (PdCl₂, SigmaAldrich, 99%) and 4.80 mg of silver nitrate (AgNO₃, Stream Chemicals, 99.9%), which were manually milled in an agate mortar until the mixture was homogeneous. Afterwards, 90 mg of sodium borohydride (NaBH₄, J. T. Baker 98%) was incorporated to the reaction mixture and it was kept under milling, until the initial red powder turned dark grey. In order to obtain a slurry-like reaction mixture, a few drops (*ca.* 0.2 - 0.5 mL) of argon-purged methanol (Ar, Praxair Inc., 99.998%; CH₃OH Merck, 99.95%) were added as liquid-phase assistant, following the liquid-assisted mechanochemical pathway. [**36**]

The synthesis process is achieved by simultaneous chemical reduction reaction of both metals precursors, using $NaBH_4$ as reducing agent, which has been extensively exploited for the metal nanoparticles synthesis. [**37-39**] The borohydride oxidation reaction has been described as a complex eight-electron transfer process, such kinetics and mechanistic pathway depend on several variables, such as pH, the nature of catalyst, and temperature. [**40**] Nevertheless, it has been also reported the occurrence of competitive processes, such as borohydride hydrolysis and reduction-oxidation of the byproducts; in this context, Glavee and coworkers have proposed that the process of borohydride oxidation for metal ions reduction can be represented by: [**41**]

$$2 BH_4^- + 2 H_2 O \rightarrow 2 B(OH)_3 + 7 H_2 + 2e^-$$

Is worth to mention that the above borohydride ion reaction is proposed in aqueous media. Nevertheless, as our case, it could be achieved in presence of alcohols (*R-OH*) instead. Released electrons are exploited for Pd^{2+} and Ag^{+} reduction reactions, disposed in proportions yielding the alloy formation in a $Pd_{1-x}Ag_x$ composition:

$$(1-x)Pd^{2+} + 2(1-x)e^{-} \rightarrow (1-x)Pd$$

 $xAg^{+} + xe^{-} \rightarrow xAg$

Thus, the overall synthetic process can be proposed as:

$$(2-x)BH_4^- + (1-x)H_2O + (1-x)Pd^{2+} + xAg^+ \to (2-x)B(OH)_3 + \frac{7}{2}(2-x)H_2 + Pd_{1-x}Ag_x + \frac{7}{2}(2-x)H_2 + \frac{7$$

Where *x* can be then interpreted as the silver content in the alloy. For this work, x = 0, 2, 5 and 10 (as at %).

2.2.Characterization

X-ray diffraction data (XRD) was collected in a Bruker *D2 PHASER* diffractometer, using Cu K_{α} radiation (λ = 1.5406 Å), operating at 10 mA and 30 kV with an scanning rate 0.36 degree/min and equipped with a Nifilter for Cu K_{β} radiation and with a θ - θ configuration. High-Resolution Transmission Electron Microscopy (HR-TEM) observations were carried out in a JEOL ARM 200 F microscope operating at 200 kV. Magnetic properties for all the nanoalloys were measured in a Quantum Design Physical Property Measurement System (PPMS) Evercool-I, using the vibration sample magnetometry module, whereas the ZFC-FC curves were obtained in a Quantum Design Magnetic Property Measurement System (MPMS-3) SQUID magnetometer. X-ray photoelectron spectroscopy (XPS) measurements were performed in a Physical Electronics VersaProbe II spectrometer, using Al K_{α} monochromatic radiation.

3.RESULTS AND DISCUSSION

Powder X-Ray diffractograms for the $Pd_{100-x}Ag_x$ nanoalloys are displayed in **Fig. 1**. For pure Pd sample, all the peaks match with the reported positions for this metal (according to ICDD file # 46-1043). The observed peak broadening is indicative of a small crystallite size; the average crystallite size (*D*) calculated by Scherrer formula resulted of 13 nm. For the case of Pd-Ag bimetallic samples, the observed peaks are considerably broader than those of pure Pd, which reflects a crystal size diminution confirmed by Scherrer formula, yielding average *D* values between 6.2 and 7.8 nm (**Table 1**). The average crystallite size for the bimetallic samples remains fairly constant, below 10 nm, across the compositional series, which reflects the excellent reproducibility and feasibility of the synthetic method.

A slight shift towards lower 20 values can be observed for the nanoalloys patterns, which can be ascribed to a subtle lattice deformation provoked by the incorporation of the silver atoms into the Pd lattice and then, ascribed to the formation of an alloyed phase. It can be also observed that for the bimetallic samples, this shift exhibits a composition-dependent behavior; particularly, a slight enlargement of the lattice parameter between 0.38 % and 0.53 % (relative to the pure Pd unit cell) as the silver concentration increases; *i.e.*, such enlargements follow a Vegard's law-like tendency (XRD patterns of Pd_{100-x}Ag_x nanoalloys were subjected to Rietveld refinement process, as shown in **Fig.S2**). The observed lattice deformation clearly suggests the formation of substitutional PdAg nanoalloys for all studied Ag contents. Further support to the formation of Pd-Ag solid solutions is given in **Fig.S3**, for which the physical mixture of 98% at Pd and 2% at of Ag presents a distinctive peak distribution compared with the diffractogram of the Pd₉₈Ag₂ nanoalloy. Summary of structural data is displayed in **Table 1**. An additional feature to be mentioned is that for nanoalloys, the broadening of peaks is asymmetric, which can be associated to a non-identical Ag distribution in every particle, giving rise to the possibility of the coexistence of nanoparticles with concentrations of Ag slightly different to the aimed stoichiometric content.



Fig. 1. XRD patterns for the $Pd_{100-x}Ag_x$ nanoalloys (x = 0, 2, 5 and 10).

Table 1. Structural data for the Pd _{100-x} Ag _x nanoalloy	ys: unit cell parameter <i>a</i> , variation	of unit cell parameter
$(a-a_{Pd})/a_{Pd}$ (relative to pure Pd) and average crystallite	e size D (Scherrer formula)	

	a (Å)	(a- a _{Pd})/a _{Pd} (%)	D (nm)
Pd	3.895	-	13.7
Pd98Ag2	3.910	0.385	7.3
Pd95Ag5	3.912	0.436	6.2
Pd90Ag10	3.916	0.539	7.8

High Resolution Transmission Electron Microscopy (HRTEM) images for the $Pd_{98}Ag_2$ nanoalloy are displayed in **Fig.2**, for which well-defined spherical-shape particles are visible showing a Gaussian-like size distribution, with a narrow standard deviation centered at 4 nm (**Fig. 2b**). This particle size is consistent with XRD results. Furthermore, the as-obtained nanoparticles exhibit high crystallinity, as indicated by HRTEM images and the corresponding Fast Fourier Transform (FFT) shown in **Fig. 2c-d**. The interatomic distances indicated by FFT correspond to {200}, {211} and {220} family planes of the fcc structure of the host Pd crystal structure with a slightly enlarged lattice parameter.



Fig. 2. For the $Pd_{98}Ag_2$ nanoalloy: a) Bright Field HRTEM image b) Corresponding nanoparticle size distribution histogram; c) Amplification of the framed zone in a) and d) corresponding FFT.

In addition, High-Angle Annular Dark-Field (HAADF) STEM images for the Pd₉₈Ag₂ nanoalloy are shown in **Fig. 3a**. This nanoalloy exhibits chemical homogeneity for the couple of nanoparticles displayed in **Fig. 3b** (Bright Field image). Complementary, chemical composition determination (**Fig.3c**) confirms the chemical content of Pd and Ag for the nanoalloy. This chemical analysis was performed by means of EDS elemental profile with Pd (L) and Ag (L) characteristic lines, which in turn was taken along the green line crossing the particles pair shown as inset in **Fig. 3c**.



Fig. 3. HR-TEM images for the $Pd_{98}Ag_2$ nanoalloy in **a**) HAADF mode and **b**) bright-field mode, showing a small cluster of two nanoparticles and **c**) EDS elemental profile, Pd (L) and Ag (L), along the green line crossing the particle shown within the inset.

In order to verify the effect on the electronic structure of the $Pd_{100-x}Ag_x$ nanoalloys caused by the incorporation of silver atoms into the crystal structure of Pd, measurements of the valence-band in XPS were performed. Fig.4 displays XPS spectrum for all the samples. For pure Pd nanoparticles, a sharp cut-off of the 4*d* band at the Fermi energy is manifested, with its centroid located at 2.3 eV, which is consistent with XPS and Ultraviolet Photoemission Spectroscopy (UPS) measurements of Pd nanoparticles previously reported by other groups [42, 43].



Fig.4. High-resolution X-ray photoelectron spectra of valence-band region for Pd_{100-x}Ag_x nanoalloys.

For the case of $Pd_{100-x}Ag_x$ nanoalloys, their corresponding spectra indicates the formation of a shoulder at approximately 5.5 eV, together with the centroid of the Pd 4d band slightly shifted towards higher E_B values as the silver content increases. The resulting profile in the spectra can be attributed to the tendency of the Ag

to transfer electrons to the 4*d* Pd band following the incorporation of silver into the Pd structure, *i.e.* the alloy formation; a similar effect has been observed for the system Pd-Al. [42] In fact, as can be seen in Fig.4, for the case of $Pd_{98}Ag_2$ sample, the relative intensity of this shoulder seems to be higher in comparison with the remaining nanoalloys. This suggests that a larger contribution of silver to the 4*d* band of palladium within the alloy is occurring for this composition, followed by a decrease for $Pd_{95}Ag_5$ and a subsequent growth as the silver contents increases further. It has been reported that when palladium is alloyed with a metal with a full *d*-band, non-exceeding Fermi level, like silver, the palladium *d*-band gains electronic charge and the occupation in the 4*d* band in the alloy increases [44]. However, the maximum of this band is displaced to energies lower than the Fermi level [44]. This charge transfer has a significant influence on the magnetic response of $Pd_{100-x}Ag_x$ nanoalloys, as will be described below.

Room temperature measurements of magnetization M as a function of applied field H were carried out for Pd_{100-x}Ag_x nanoalloys. A clear paramagnetic response associated to the linear M-H plots is observed in Fig.5 for all the studied compositions, indicating the presence of a magnetic moment per unit volume for pure Pd nanoparticles as well as for each Pd-Ag nanoalloy. Maximum magnetization, M_{max} (corresponding to the value of M at 10 000 Oe) decreases for Pd₉₈Ag₂ nanoalloy (relative to pure Pd sample), followed by a partial recovery for the 5 at% Ag-containing sample and a subsequent decrease for the Pd₉₀Ag₁₀ composition. Summary of magnetic properties of the Pd_{100-x}Ag_x compositional series is displayed in Table 2.



Fig. 5. Magnetization *M*-*H* curves for $Pd_{100-x}Ag_x$ nanoalloys samples at 300 K.

Presence of magnetic moment per atom in transition metals can be explained in terms of the Stoner criterion [6]. According to this criterion, the key parameter to develop magnetic moment is a high density of states at the Fermi level, for which metals like Fe, Co and Ni accomplishes very well, yielding ferromagnetic ordering at room temperature in addition to magnetic moment per atom. For the case of Pd, the Stoner criterion is barely accomplished [8,10], allowing the presence of magnetic moment without ferromagnetic ordering at room temperature, as confirmed by *M*-*H* measurements of Fig.5. On the other hand, the susceptibility per mass χ_m (measured as the slope for each *M*-*H* curve of Fig.5) also exhibits an initial decrease for the Pd₉₈Ag₂ sample (from 3.6 x10⁻⁶ -pure Pd- to 1.6x10⁻⁶ emu/gOe), followed by a partial recovery for Pd₉₅Ag₅ (up to 2.3x10⁻⁶ emu/gOe) and a subsequent marked reduction as the silver contents increases further (1.1x10⁻⁶)

emu/gOe). Summary of magnetic properties for $Pd_{100-x}Ag_x$ nanoalloys is displayed in **Table 2**. This observed tendency for χ_m is consistent with the tendency of Ag to transfer electrons to the *d* band of Pd for PdAg nanoalloys, as indicated by XPS results (**Fig. 4**), since for the $Pd_{98}Ag_2$ sample, a *d* band with more electrons will imply a reduction on the resultant magnetic moment and hence, a reduced susceptibility. For the $Pd_{95}Ag_5$ nanoalloy, the transfer of electrons to *d* band of Pd is lower, which affords the recovery of the magnetic moment and, finally, for the $Pd_{90}Ag_{10}$ sample, the significant reduction of χ_m can be ascribed to the higher content of Ag, which at this point produces a dilution effect of the magnetic moment.

Complementary, the magnetic response for the $Pd_{100-x}Ag_x$ nanoalloys as a function of temperature was explored by means of thermo-magnetization measurements shown in **Fig. 6** and **Fig. 7**. Both Figures display the Zero-Field-Cooled (ZFC) and Field Cooled (FC) magnetization curves, as well as the $1/\chi_m$ as a function of temperature for all the nanoalloys. For the pure Pd nanoparticles (**Fig.6**), ZFC and FC are separated, reaching a maximum around 110 K for the ZFC, indicating a magnetic transition from paramagnetic to ferromagnetic ordering, as confirmed by low-temperature magnetization curves shown in a subsequent section. Complementary, the $1/\chi_m$ curve exhibits a linear, Curie-like behavior for T > 150 K, which confirms the paramagnetic state observed by *M-H* measurements at room temperature. Fitting of Curie's Law for this data range indicate a magnetic moment of 1.96 µ_B per Pd atom (**Table 2**). Below 150 K, separation of $1/\chi_m$ curve from linear tendency is consistent with the magnetic transition occurring at 110 K.



Fig.6. For pure Pd nanoparticles: **a**) Zero-field-cooled (ZFC) and field cooled cooling (FC) magnetization curves and **b**) $1/\chi_m$ curve (all taken at 100 Oe of applied magnetic field).

For the nanoalloys (**Fig.7**), the $1/\chi_m$ curves also exhibit a Curie-like behavior for T > 150 K (**Fig.7b**), together with a deviation from linear regime for T < 150 K, for which a magnetic order-disorder transition can be associated. Fitting of Curie's Law for the temperature interval above 150 K indicates a reduction (relative to pure Pd nanoparticles) of the magnetic moment for the Pd₉₈Ag₂ nanoalloy (0.92 µ_B), followed by a recovery for the Pd₉₅Ag₅ sample (1.57 µ_B). A subsequent diminution (down to 1.13 µ_B) was recorded for the Pd₉₀Ag₁₀ nanoalloy. Summary of magnetic moment data is given in **Table 2**. This tendency of the magnetic moment per Pd atom as a function of Ag content for $Pd_{100-x}Ag_x$ system is consistent with the observed magnetic susceptibility variation of **Fig.5**. In addition, for all the compositions, a slight upturn can be observed in low-temperature range (below 50 K), which can be attributed to magnetic moments of Pd atoms that are not magnetically frozen, even at very low temperatures (i.e. below 25 K), exhibiting a Curie-like tail [45].



Fig. 7. For $Pd_{100-x}Ag_x$ nanoalloys: **a)** Zero-field-cooled (ZFC) and field cooled cooling (FC) magnetization curves and **b)** $1/\chi_m$ curve at (all taken at 1 kOe of applied magnetic field).

	M _{max} 300 K (10 ⁻³ emu/g)	χm 300 K (10 ⁻⁶ emu/gOe)	<i>Н</i> с 5 К (Ое)	μ (μ _B)
Pd	34.25	3.6	25	1.96
Pd ₉₈ Ag ₂	16.22	1.6	168	0.92
Pd ₉₅ Ag ₅	22.42	2.3	80	1.57
Pd ₉₀ Ag ₁₀	4.26	1.1	25	1.13

Table 2. Magnetic properties for $Pd_{100-x}Ag_x$ nanoalloys: Maximum magnetization M_{max} (at H = 10 kOe), mass susceptibility χ_m , coercive field H_c and magnetic moment μ per Pd atom.

Furthermore, *M*-*H* measurements at very low temperature (5 K) for the $Pd_{100-x}Ag_x$ nanoalloys are shown in Fig. 8. As can be seen, pure Pd presents a slight hysteretic behavior (associated with a small coercivity of 25 Oe) overlapped with a predominant linear paramagnetic response. Complementary, M-H plots for the Pd-Ag nanoalloys exhibit a more defined hysteretic response, characterized by a distinctive coercive field H_c varying within the range 25 - 168 Oe (Table 2), which clearly reflects the development of a ferromagnetic ordering. Ferromagnetism should be associated to inner atoms within each nanoparticle, for which well defined crystallinity favors the development of magnetic moments according to the Stoner criterion. On the other hand, the concomitant paramagnetic response comes from a layer of surface disordered atoms, also known as "magnetic dead layer" (MDL) [46-49], which precludes the saturation of the magnetization for all Pd_{100-x}Ag_x compositions. For the case of a coexisting ferromagnetic core with MDL, the core dominates the low-field *M*-*H* response of the whole sample, thus producing a characteristic ferromagnetic behavior [47]. In this sense, a maximum H_c value of 168 Oe was observed for the Pd₉₈Ag₂ nanoalloy, followed by a decreasing tendency as the Ag content increases (See Table 2). The significant values of coercivity observed for these $Pd_{100-x}Ag_x$ nanoalloys can be attributed to surface anisotropy, in particular for the $Pd_{98}Ag_2$ nanoalloy having the highest coercivity value of 168 Oe. According to XPS results, this nanoalloy presents a large charge transfer from silver to the 4d band of Pd, which favors the spin-orbit coupling (since the interaction energy of the spin-orbit coupling is proportional to the number of electrons of magnetic atoms [50]) and hence, a high magnetic anisotropy (which in turns depends on the strength of the spin-orbit interaction). For the remaining compositions, decreasing H_c values are consistent with decreasing spin-orbit interaction induced by reduced charge transfer associated to increasing silver content, x. Similar magnetic characteristics depending on surface anisotropy and spin-orbit interaction have been reported for cobalt nanostructures [46] as well as for Platinum nanoparticles [13, 14].



Fig.8. Magnetization *M*-*H* curves for $Pd_{100-x}Ag_x$ nanoalloys at 5 K.

5.CONCLUSIONS

Mechanochemical reduction method is a successful low-solvent procedure to synthesize Pd-Ag bimetallic nanoparticles by using soft conditions at room temperature, allowing the obtaining of nanoparticles with narrow size distribution without capping agents. Structural and crystal characterization of all the samples clearly indicates the formation of a nanoalloyed Pd-Ag phase. Magnetic measurements showed that pure Pd nanoparticles, as well as $Pd_{100-x}Ag_x$ nanoalloys (x = 2, 5, 10) are paramagnetic at room temperature, together with a decreasing magnetic susceptibility associated to a dilution effect provoked by the progressive silver atoms incorporation into the Pd lattice. At very low temperature (5 K), magnetization measurements demonstrate ferromagnetic ordering for all the compositional $Pd_{100-x}Ag_x$ series, characterized by distinctive coercive fields between 25 – 168 Oe.

ACKNOWLEDGEMENTS

V.F.R-R. and R.D-P. thank *CONACyT* for the Ph.D. and Sc.M. scholar fellowships, respectively (numbers 271406 and 290941). I. Betancourt thanks *DGAPA-UNAM* for research support by *PAPIIT* project IN-114819; D.D. thanks FQ-UNAM (*PAIP* 5000-9039). I.Z.-D. is grateful for the postdoctoral fellowship awards from CM-SECITI/095/2017 project. The authors also acknowledge Josué Romero (IIM-UNAM) for helping with HR-TEM experiments, as well as Lázaro Huerta (IIM-UNAM) for XPS experiments.

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Supplementary Material

Magnetic Properties of Pd-Ag Nanoalloys Obtained by Mechanochemical Synthesis

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Figure S1 shows a graphical representation on Stoner criterion, $U \cdot g(E_F)$ as a function of atomic number, *Z* for *3d* (red) and *4d* (green) bulk metals (*U* represents Coulomb energy and $g(E_f)$ is the density of states per atom at Fermi level) [1]. For Fe, Co and Ni, the Stoner criterion $U \cdot g(E_F) \ge 1$ confirms a ferromagnetic behavior, whereas for Pd, such criterion is close to be fulfilled. For Ag atoms, $U \cdot g(E_F) << 1$ is consistent with its diamagnetic behavior.



Fig. S1. Stoner criterion $U \cdot g(E_F)$ as a function of atomic number Z for bulk metals (adapted from [6]).

Figure S2 shows Rietveld refinement results obtained for XRD patterns of $Pd_{100-x}Ag_x$ nanoalloys. Rietveld refinement process was carried out with *Profex v3.11.1* software, using the BGMN program [2]. BGMN program is based on the modeling of the peak profiles by a deconvolution of wavelength distribution (A), instrumental profile (G) and real structure profile (P). The proposed crystal structure comprises a unit cell with Pd and Ag atoms, the *Fm-3m* space group and an occupation factor r = x (the stoichoimetric atomic composition). Intensities and lattice constant were taken as the parameters for refinement process. Refinement results of Pd₉₈Ag₂, Pd₉₅Ag₅ and Pd₉₀Ag₁₀ diffractograms show a shallow increase of the lattice parameters as a function of silver concentration. This lattice variation lie within the range 0.38 % - 0.53 % (relative to the pure Pd crystal structure). The observed lattice deformation reflects the formation of substitutional Pd-Ag solid solution across the compositional Pd_{100-x}Ag_x series.



Fig. S2. Rietveld refinement results obtained for XRD patterns of Pd₉₈Ag₂, Pd₉₅Ag₅ and Pd₉₀Ag₁₀ nanoalloy samples.

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Figure S3 shows the diffractogram for a physical mixture of 98% at Pd and 2% at of Ag, together with the $Pd_{98}Ag_2$ nanoalloy. The observed peak distribution clearly suggests the formation of Pd-Ag nanoalloys, since both Pd and Ag phases can be clearly identified in the mixture, unlike the diffractogram for the $Pd_{98}Ag_2$ nanoalloy, which exhibits no segregation of Pd or Ag atomic species.



Fig. S3. XRD diffractograms for the Pd₉₈Ag₂ nanoalloy and the physical mixture of Pd and Ag nanoparticles in the same proportion. No segregation of Pd or Ag atoms is manifested for the Pd₉₈Ag₂ nanoalloys.