Surface & Coatings Technology 205 (2011) 4934–4940

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

On the use of radioisotopes to study the possible synthesis by magnetron sputtering of bimetallic nanoparticles

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ARTICLE INFO

Article history:
Received 16 February 2011
Accepted in revised form 19 April 2011
Available online 27 April 2011

Keywords:
Magnetron discharges
Nanoparticles
Radioisotopes

ABSTRACT

An approach using physical vapor deposition technology to produce nanoparticles (NPs) containing radioactive atoms and the methodology to transfer them in pure water is investigated. NPs are synthesized by magnetron sputtering at high pressure and radioactive atoms are loaded on magnetron cathodes prior to sputtering. The technique was tested for gold cathode loaded with $^{57/58}$Co and $^{195/196}$Au. Linked to biological vector molecules, the nanoparticles can be used to enhance diagnostic sensitivity in medical imaging or to treat cancer.

Sizes and morphologies of the NPs were analyzed by electron microscopy, UV-Visible spectroscopy and atomic absorption spectroscopy. Results show well dispersed NPs with sizes varying between 5 and 10 nm. Activities of these NPs were measured with a CAPINTEC well counter and a High Purity Germanium detector system. Centrifugation analyses also demonstrate that the choice of the activated metal which can be alloyed with NPs plays an important role in the synthesis. This was confirmed by the Au–Co phase diagram that shows that cobalt cannot be included efficiently in the gold NPs conversely to gold.

1. Introduction

We recently investigated the possibility to synthesize sub 10 nm NPs by magnetron sputtering. This technique, based on aggregation and growth in gas phase can be used to produce non-agglomerated metallic NPs with a narrow size distribution [1–5].

The technique was proposed for the first time by Takagi in 1972 to produce high quality films by ionized cluster beam (ICB) deposition [3]. Their idea was to generate a cluster beam formed by inert gas condensation (IGC) after evaporation of film materials. A few years later, Haberland et al. decided to vaporize the film material by magnetron sputtering rather than by evaporation [6]. Magnetron sputtering has the advantage to produce atomic vapor from a wide variety of solid materials or composites. Sputtering allows for the deposition of films having the same composition as target source, and when used in co-sputtering mode, one can vary the coating concentration over a large range.

In this study, we investigated the possibility to synthesize sub-10 nm Au–Co nanoparticles with a large amount of Co by magnetron sputtering. One special feature of the work is that we used radioactive Co and Au as a main investigation tool to control and to assess the production yield of NPs.

This method using radioactivity as a tool for detection is far more straightforward with respect to the traditional ones such as XPS or EDX (Energy Dispersive X-ray Analyis).

The strategy involved the synthesis and immobilization of NPs on a soluble substrate (NaCl) that is later dissolved in water. Activity evaluation of the solution and the NPs were performed after centrifugation by measuring the amount of radiation emitted either by the supernatant or the solid phase. By doing so, it is possible to evaluate if Co atoms are mixed with those of Au in the solid NPs and to examine if bulk phase diagrams of bimetallic materials are still valid for NPs as a large fraction of atoms resides on the surfaces [7]. For example, surface segregation of bimetallic NPs has already been observed in which chemical composition at surface differs from that in bulk [8–11]. Therefore, the properties of miscibility of individual

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doi:10.1016/j.surfcoat.2011.04.077

Table 1
Main characteristics and production routes of the Co and Au radioisotopes used in this study.

Radioisotope	Half life (days)	Production route	Main γ-radiations (keV)
^{57}Co	272	1 - ^{59}Co(p,p2n)^{57}Co 2 - decay of ^{57}Ni (produced by ^{59}Co(p,3n)^{57}Ni)	122 and 136
^{58}Co	71	^{59}Co(p,pn)^{58}Co	811
^{195}Au	186	1 - ^{197}Au(p,p2n)^{195}Au 2 - decay of ^{195}Hg (produced by ^{197}Au(p,3n)^{195}Hg)	99
^{196}Au	6	^{197}Au(p,pn)^{196}Au	356 and 333

elements in bimetallic NPs are questionable and change in miscibility may help to design novel alloyed NPs possessing unique properties that may not be obtained as bulk materials.

In order to ensure that NPs, when put in water solution, act as separate entities and do not aggregate together, in-situ post-synthesis functionalization with a Plasma Polymer Allylamine (PPAA) layer was performed. This treatment insures that NPs are monodispersed and stay as such for at least two weeks in the solution [5]. This delay is convenient for appropriate manipulation and measurements of radioactive solutions.

2. Experimental set up

Depositions were performed by high pressure magnetron discharge. Radioactive targetry was elaborated by depositing radioactive metallic disks (0.8 cm diameter, 100 μm thick) on a non-radioactive Au target. The radioisotopes of Co ($^{57/58}$Co) and Au ($^{195/196}$Au) used in this work were produced at the cyclotron of the Joint Research Centre, European Commission (Ispra, Italy). The cyclotron is a Scanditronix MC 40 model (K = 40) able to accelerate 4 different particles (p, d, α and $^{3}He^{2+}$) at variable energies. ^{57}Co and ^{58}Co radioisotopes are simultaneously produced by proton beam bombardment of disks of pure Co. ^{57}Co is produced via the nuclear reactions ^{59}Co(p,p2n)^{57}Co and by decay of ^{57}Ni radioisotope which is activated by the nuclear reaction ^{59}Co(p,3n)^{57}Ni while ^{58}Co is mainly produced by the reaction ^{59}Co(p,pn)^{58}Co. In the case of ^{196}Au and ^{195}Au, they are activated through proton beam bombarding disks of pure Au. ^{195}Au is activated via the reaction ^{197}Au(p,p2n)^{195}Au and by decay of ^{195}Hg which is simultaneously produced through the reaction ^{197}Au(p,3n)^{195}Hg. ^{196}Au is produced via the single nuclear reaction channel ^{197}Au(p,pn)^{196}Au.

These radioisotopes have been chosen for their suitable half life which allow us to perform relatively long term (without significant radioactive decay) experiments of stability of the produced radioactive NPs. They are also chosen for their γ − radiation which can be detected with high precision and accuracy. Table 1 presents the main characteristics of these radioisotopes including the nuclear reactions cyclotron production routes.

In both Co and Au cyclotron irradiations, several disks were prepared and irradiated in a single cyclotron irradiation run of several hours. Considering the optima cross sections of the mentioned nuclear reactions for high radioisotope production yields, proton beam energies of 32 and 30 MeV were used for Co and Au targets respectively. The Co and Au disks respectively were put in an Al capsule which was inserted into a target holder equipped with a water cooling system to avoid over heating of the disks during the cyclotron irradiations. Fig. 1 presents a schematic design of the water cooled target system.

During the irradiations, the beam intensity was monitored via a Faraday cup on which the target was mounted. After the end of each irradiation, several days of radioactive decay were necessary to allow the dose rate to reduce somewhat and allow handling of the activated samples at minimum radiation exposure to the workers. Considering the cross-section and the energy loss, the disks were activated homogeneously all over their thicknesses.

The disks were then shipped to Belgium and inserted into the deposition equipment that is presented in Fig. 2. A turbomolecular pump is used to obtain a base pressure of 10^{-4} Pa. The chamber is equipped with a magnetron sputtering source and a thermal evaporation source. The latter consists of a tantalum evaporation boat source filled with NaCl grain (99.9% purity) and maintained between 2 clamps connected to AC current (i ≅ 80A and V ≅ 3 V). A Quartz Crystal Monitor (QCM) is mounted near the sample on the substrate holder for monitoring the amount of NaCl deposit. The Au

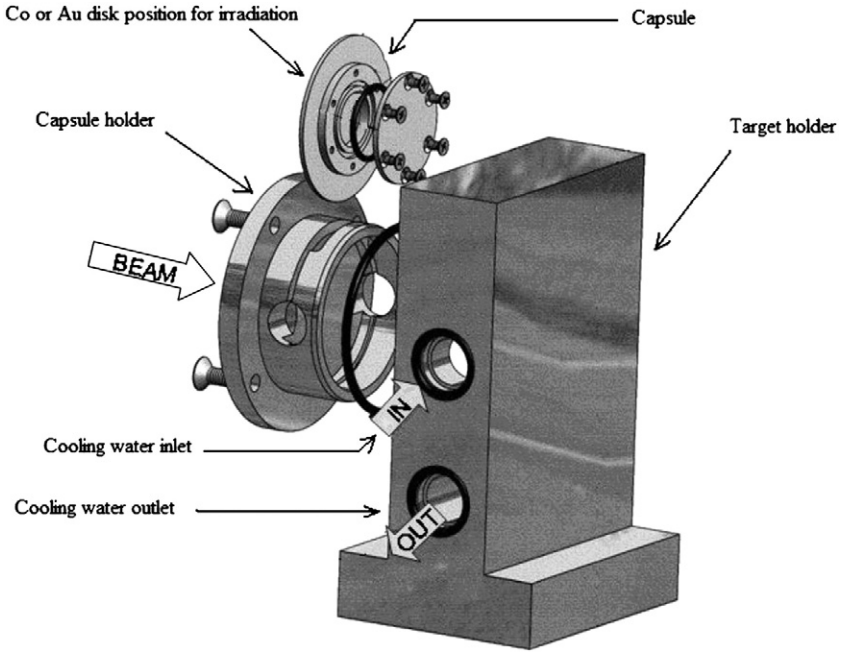

Fig. 1. Schematic design of water cooled target system used to perform disk activation.