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Facile synthesis of metastable Ni–P nanostructured materials by a novel bottom-up strategy

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ABSTRACT

A novel bottom-up strategy combining chimie douce and non-conventional consolidation process to elaborate Ni–P metastable alloy is described here. The chimie douce method consists on the polyol process, modified by the addition of hypophosphite (strong reducing agent). It allows elaborating Ni–P nanopowder. The consolidation of the as-obtained nanoparticles is carried out by Spark Plasma Sintering (SPS). The microstructure of the powder and nanostructured dense sample was studied and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive X-ray (EDX), thermogravimetric analysis (TGA), differential thermal analysis (DTA) and FTIR spectroscopy. The nanopowder is formed of the metastable Ni–P alloy, with a composition of about 3.44% in phosphorus. Unlike Ni–P alloys prepared by electroless or electrodeposition, the nanoparticles developed show good crystallinity. They have spherical morphologies with a size of about 100 nm and are formed by aggregation of crystallites about 8 nm in diameter. Various analysis techniques showed that SPS treatment induced the transformation of the metastable Ni–P alloy in a two phases: almost pure nickel and a new phase with chemical formula Ni_3P. This latter is in form of spherical particles with about 130 nm in diameter, while the nickel grains have a polygonal shape with 330 nm in diameter.

1. Introduction

Since the pioneer work of Gleiter [1] on nanostructured materials, several works have been devoted to these emerging materials. Indeed such class offers often superior and sometimes new mechanical and functional properties in comparison with corresponding coarsened-grain materials. These enhanced properties are mainly due to the small grain size which leads to a large amount of atoms located in or near the grain boundary. Depending on the grain size this amount can exceed that inside the grain [2,3].

Among these materials, nanostructured metals or alloys based on the 3d elements are still subject of great interest due to their various potential industrial applications. As far as nanostructured nickel based materials are concerned, numerous applications can be cited: semiconductors, catalysts [4–6], microelectronic devices, Micro Electromechanical Systems (MEMS), aircraft engines and the hot end components of various types of gas turbines [7].

It should however be noted that pure nanostructured nickel suffers from a lack of thermal stability and abnormal grain growth [8]. Thus pure nanostructured nickel is replaced by Ni-based alloys with several additional elements depending on the sought property. For instance nickel–phosphorus alloys are well known as corrosion-resistant, wear-resistant, wear-resistant coating on hard-disk substrates and for catalytic purposes as well [9,10].

These nanostructured Ni–P alloys are mainly elaborated by two methods. Electrodeposition method is carried out by use of an electrolytic bath containing nickel salt and phosphorous acid. Nano-crystallite film of Ni–P is deposited onto a substrate Ti for instance by applying a current density to the system, pure nickel being the soluble anodic material [11]. The second method consists on an electroless deposition. In this case, a chemical reducing agent such as hypophosphite is used instead of electrical energy. The reduction occurred in a bath aqueous solution in which nanostructured Ni–P film is deposed on a given substrate [12–14].

Several works have been devoted to investigate the mechanical

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properties of the as-obtained films along with their heated counterparts. They show that annealed Ni–P alloys have very high hardness and can be used as wear-resistant coatings. However these materials are subject to severe brittleness that makes difficult their workability.

The present works brings a new contribution dealing with the system Ni–P. Whereas the reported works are devoted to nanostructured Ni–P films elaborated by electro or electroless deposition, the present paper concerns bulk nanostructured Ni–P material elaborated by a new bottom-up strategy combining chimie douce and rapid consolidation process. The chimie douce refers to a chemical reducing process conducted in a polyol medium [15–18]. It allows elaborating metastable Ni–P alloy in powder form with nanoparticles having controlled size. When these nanopowders are consolidated by the rapid process namely Spark Plasma Sintering, bulk dense pieces with limited grain growth are obtained.

2. Experiments

2.1. Synthesis

The powder has been prepared according the general procedure described in our previous work [19]. Nickel (II) acetate tetrahydrate (Prolabo), sodium hydroxide (Prolabo) were dispersed in a given volume of ethyleneglycol (EG) (250 mL), with a metal concentration of 0.08 M and sodium concentration of 0.262 M. The reducing effect of polyol is amplified by adding sodium hypophosphite a strong reducing agent with the ratio $R = [NaH_2PO_2]/[Ni(OAc)_2\,4\cdot H_2O] = 3$. The mixture is heated at the boiling temperature of the polyol (196 °C).

As it was shown, the synthesis of metal in polyol medium results from a reduction reaction which is favored when water is eliminated from the medium: the hydrolysis ratio defined as $h = n(\text{water})/n(\text{metal})$ must be set at $h = 0$ [20]. Thus water coming from the metal acetate and the solvent was distilled and the reaction was let to proceed for 2 h. The precipitate obtained is separated from the liquid by centrifugation, washed several times with ethanol and then with acetone, and finally dried at 50 °C in an oven.

Before being consolidated, the powders were heated under hydrogen at 300 °C during one hour. This allows to eliminate organic molecules and to reduce all trace of nickel oxide present on the surface of the particles.

The bulk sample was processed by Spark Plasma Sintering route (SPS) using a Syntex society model 515S apparatus, located at the ICMPE platform (Thiais). After establishing a primary vacuum and passing an argon flow into the apparatus, a uniaxial pressure and a high-pulsed DC current were applied to the cylindrical graphite die containing the powder placed between two electrodes. The powder was held under a pressure of 53 MPa at 600 °C for 10 min. After SPS, disk of 10 mm in diameter and 3 mm in thickness was obtained.

2.2. Characterization techniques

X-ray diffraction (XRD) using CuKα radiation ($\lambda = 0.15406$ nm) was performed to identify the phases that were present. The patterns were recorded in transmission mode (PHILIPS PW2216:20), in the range 30–100° (2θ) with a scan step of 0.04° (2θ) and a step duration of 15 s. Different crystalline phases were identified using Match software [21]. The crystallite size has been calculated using the Scherrer formula.

The particles size and morphology and the microstructure of the powder and the consolidated samples were studied using a JEOL-2011 transmission electron microscope (TEM) operating at 200 kV. EDX analyses have been conducted on electron microscope H9000 NAR. Technical EDX atomic percentage was determined by analyzing the lines Kα1 of P and Ni elements located respectively at 2.0 keV and 7.477 keV.

The phosphorus content in the samples was determined by ICP measurements which require dissolving the samples in a mixture of acids ($HF–H_2SO_4$) in Teflon crucibles.

The powder was also examined by thermogravimetric and differential thermal analysis (TGA-DTA) in a Perkin–Elmer apparatus at a heating rate of 10 °C/min between 20 °C and 650 °C using argon as purge gas.

The Fourier transform infrared (FTIR) spectrum of the Ni–P sample was recorded on a Bruker Spectrophotometer within the wave number range of 400–4000 cm^{-1}. The samples were prepared in the form of a pellet by mixing the material with potassium bromide (KBr).

3. Results

3.1. Chemical analysis by ICP and EDX

The ICP chemical analysis of the starting powder and the sintered sample revealed in addition to nickel, the presence of the phosphorus derived of sodium hypophosphite. The weight percentage of phosphorus is 3.44% and 4.01% for the powder and the bulk sample, respectively.

A further study was performed by Energy Dispersive X-ray (EDX) analysis of the nanometric powders (as-prepared and pre-treated) (Fig. 1a and b). This Analysis confirmed that beside nickel, phosphorus is present in the as-prepared powder as well as and in the pre-treated one with a percentage of 3.52% and 3.86%, respectively. These values are in good agreement with that obtained by ICP chemical analysis method.

On the other hand we notice in the case of the as-prepared powder the existence of carbon and oxygen elements with percentages not exceeding 1%. These chemical elements derived from the presence of organic molecules that are adsorbed on the surfaces of the particles, their presence was confirmed by thermogravimetric analysis (TGA) analysis and by FTIR. Heating the powder at 300 °C under H_2 (pre-treated) led to the departure of C and oxygen (Fig. 1b).

3.2. X-ray diffraction characterization

The XRD patterns of as-prepared and pre-treated powders are similar with that of pure nickel (Fig. 2a and b). The refinement of these diffractograms using Fullprof program "whole-pattern Fitting" mode has shown that these compounds crystallize in the cubic face-centered system with lattice parameter ($a = 3.5245(2)$ Å and $a = 3.5251(3)$ Å) very close to that of pure nickel (JCPDS No. 04-0850, $a = 3.522$ Å).

It should also be noted that the metal particles are not oxidized since no trace of nickel oxide was observed in the XRD diffraction pattern (detection limit ~ 2%). This is certainly due to the presence of organic residues (polyol) that remained adsorbed at the particle surface, inhibiting its oxidation as frequently noted in the literature [22,23].

The diffraction pattern of the X-ray bulk sample obtained by consolidation of the powder of Ni–P shows the presence of low intensity peaks represented by (*) in the XRD diffractogram (Fig. 2c). By identification, these peaks can be attributed to the Ni_3P phase (JCPDS card No. 00-034-0501). This phase was formed during the consolidation step and derives from the use of sodium hypophosphite (reducing agent in the synthesis process).

The grain growth during the heat treatment by SPS is accompanied by a narrowing of the peaks in the XRD diffractograms. The crystallite size is estimated by applying the Scherer formula. In this