

Dendritic Ag–Fe nanocrystalline alloy synthesized by pulsed electrodeposition and its characterization



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ARTICLE INFO

Article history:

Received 3 June 2014

Received in revised form 4 August 2014

Accepted 7 August 2014

Available online 15 August 2014

Keywords:

Ag–Fe nanoparticles

Nanocrystalline alloy

Dendrite morphology

Pulsed electrodeposition

Microstructure

Magnetic materials

ABSTRACT

Synthesis of dendrite shaped Ag–Fe alloy nanomaterial by pulsed electrodeposition route was investigated. The alloy samples were deposited at different current densities from electrolytes of different compositions to study the influence of current density and bath composition on metal contents in the alloy, which was determined by ICP-OES analysis. The XRD studies were carried out to determine the structure of these samples. Magnetic characterization at room temperature and during heating was carried out to understand their magnetic behaviour and to confirm the inferences drawn from the XRD results. The XPS spectra proved the presence of Fe and Ag in the metallic form in the alloy samples. The FESEM and TEM micrographs were taken to view the surface morphology of the nanosized particles.

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1. Introduction

Ever since the discovery of giant magneto resistance (GMR) in nanocrystalline magnetic materials with large anisotropy, synthesizing such materials in different combinations by different methods and investigating their properties have become an important area of research. Magnetic properties of transition metals can be altered and their stability can be improved by alloying them with noble metals. Nanocrystalline Fe–Cu, Fe–Ag, Co–Ag, etc., exhibit higher anisotropy and hence show greater GMR [1–4]. At the same time, systems like Fe–Ag and Co–Ag are thermally immiscible as per their phase diagrams under equilibrium conditions [5,6]. In the case of Ag–Fe the solid solubility is insignificant and that in the liquid state is very low. This is due to the large positive heat of mixing, which is 42 kJ/mol in the solid state at equiatomic composition and 28 kJ/mol in liquid state [7]. Though this system has been prepared by a few methods such as magnetron sputtering, pulsed laser deposition, vapour quenching, sol–gel method, molecular beam epitaxy, etc., and its properties investigated [8–12], reports on its electrodeposition are scarce. The stability of electrodeposited Ag–Fe alloy has

been reported by Roy et al. [13]. In this work dendrite shaped Ag–Fe alloy nanomaterial is prepared in different compositions by pulsed electrodeposition at different current densities from electrolytes not reported so far.

2. Materials and methods

Electrodeposition is one of the best suited 'bottom-up' approaches for synthesizing alloy nanomaterials with high purity. The metals forming the alloy can be deposited simultaneously after optimization of the parameters such as the current density, bath composition, pH, addition of complexing agents, temperature, etc. Since Ag and Fe are two metals with a large difference in their standard electrode potentials, their simultaneous deposition to form an alloy, can be carried out in the presence of a complexing agent which reduces the standard electrode potential of the more noble metal. The standard electrode potential of Fe (–0.44 V) is far below that of Ag (+0.799 V). Hence the complexing agent, thiourea (0.05 M) was added to the electrolyte along with 0.2 M of sodium gluconate which served as the additive agent. The electrolyte contained 0.01 M of AgNO₃ with 0.05 M of Fe(NO₃)₃ for bath 1 in which the metal salts ratio was 1:5 and 0.01 M of AgNO₃ with 0.1 M of Fe(NO₃)₃ for bath 2, having the ratio of 1:10. Sodium perchlorate (0.2 M) was added to the bath in order to improve the ionic conductivity and enhance deposition. As the pH of the bath was very

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low, it was increased to 4 before every deposition by adding a few drops of diluted ammonia.

The pulse currents of densities of 30 mA/cm², 40 mA/cm² and 50 mA/cm² were passed through the electrolyte with 1 ms T_{on} and 9 ms T_{off} at a duty cycle of 10% to deposit samples 1A, 1B, 1C from bath 1 and 2A, 2B, 2C from bath 2. Passage of pulse current not only ensures uniform distribution of ions before every pulse during T_{on} , but also enables fresh nucleation during the ON time and formation of nanosized particles. The bath was stirred continuously using a magnetic stirrer. A stainless steel substrate was used as the cathode while a graphite plate formed the anode. This is a slightly modified method of what has been reported by the authors for the synthesis of Ag–Ni alloy nanomaterial [14].

The structure of the deposits were investigated using a Rich Siefert 3000 X-ray diffractometer (XRD) with Cu $K\alpha_1$ radiation ($\lambda = 0.15406$ nm). The composition of the metals in the alloy samples was also analysed using Perkin Elmer Optima 5300 DV, ICP-OES. The field emission scanning electron microscope (FESEM) Hitachi, SU6600, equipped with energy dispersive X-ray spectrometer (EDX) was used for observing the morphology of Ag–Fe samples. The microstructure of the deposit Ag–Fe 2B was determined using the Transmission Electron microscopy (HRTEM) on a JEOL model JEM 2011 at an accelerating voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) measurements were made with Omicron ESCA Probe spectrometer with monochromatized Al $K\alpha$ X-rays ($h\nu = 1486.6$ eV). The vibrating sample magnetometer (VSM) EG&G, PARC Model 4500 was used to analyse the magnetic behaviour of the samples both at room temperature and during heating.

3. Results and discussion

3.1. Composition analysis

The ICP-OES analysis reveals the metal contents in the alloy samples deposited using different current densities from the two electrolytic compositions. These values are presented in Table 1. Samples 1A, 1B and 1C deposited from bath I, have lower Fe content compared to that in 2A, 2B and 2C obtained from bath II, as expected. It is also observed that the Fe content increases with increase in current density. The samples from bath I show wide variations in the Fe content with changes in current density, whereas the samples from bath II have the Fe at.% lying within the range, from 86.6 and 94.2 for the three current densities. Therefore at the lower bath concentration, the current density influences the metal composition drastically. But at the higher concentration of the bath, the current density seems to be less influential. Though the other parameters such as duty cycle of the current pulse, pH, temperature of the bath, the presence of additives, etc., influence the size and the morphology of the deposits in addition to having little effect on the metal contents, the bath composition and the current density are the two parameters which greatly alter the alloy composition.

3.2. Structural analysis

The XRD patterns of the samples Ag–Fe 1A, 1B, 1C and 2A, 2B, 2C are shown in Fig. 1a–c and d–f respectively. The samples 1A, 1B, 1C prepared from 1:5 composition of the electrolyte, exhibit fcc structure peaks at the same positions as fcc Ag peaks according to JCPDS file no. 893722 whereas the samples 2A, 2B, 2C obtained from 1:10 composition have a structure similar to bcc Fe (JCPDS no. 851410). In the samples deposited from bath 2, the most prominent fcc Ag(111) peak is not visible. The presence of fcc peaks can be attributed to the mixing of Fe atoms whose atomic radius

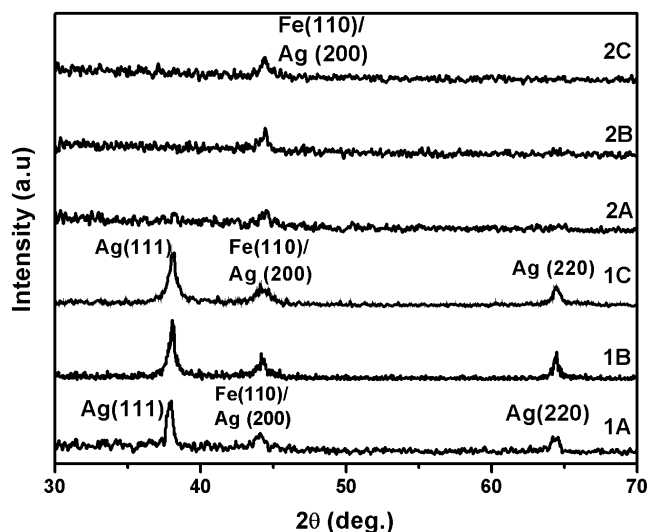


Fig. 1. XRD patterns of samples 1A, 1B, 1C deposited from bath 1 showing mixed fcc and bcc structure peaks and 2A, 2B, 2C from bath 2 showing bcc Fe peaks.

is smaller, into the fcc Ag lattice. Similar formation of fcc structure of Ag–Fe alloy nanomaterials have been reported in literatures [8,13,15]. But, since the peak positions of bcc Fe (110), (200) and (211) are very close to the fcc peaks (200), (220) and (311) of Ag–Fe alloy, they are likely to have submerged. Hence the coexistence of Fe rich bcc phase of the alloy cannot be ruled out. In the case of samples 1A, 1B, 1C deposited from lower Fe concentration in the electrolyte the fcc phase is more prominent while the samples 2A, 2B, 2C deposited from higher concentration of Fe, exhibit bcc structure (JCPDS file no. 851410). Kataoka et al. have reported fcc structure for the vapour quenched $Fe_{1-x}Ag_x$ alloy for $x > 0.6$, coexistence of fcc and bcc phases for $0.14 < x < 0.6$ and bcc peaks for $x < 0.14$ [16]. This is in close agreement with what is observed in the present study. The mixed fcc and bcc phases of the samples prepared from bath 1 and the bcc phase of the alloy samples obtained from bath 2 are confirmed by their Curie transitions.

3.3. Surface morphology

The FESEM micrographs of four samples 1A, 1B, 2A and 2B are shown in Fig. 2a–d respectively. All the samples show a beautiful leaf-like dendritic growth. Formation of dendrites is attributed to the state where there is growth of protrusion under charge transfer control while the deposition on the rest of the cathode is under diffusion control. Dendrites with ordered nanometric structures grow as branches when a critical overvoltage is exceeded. When metals are deposited at high current densities as in pulsed electrodeposition, there is a tendency to form powdered deposits which are dendritic. Factors such as decrease in concentration of the depositing ions, temperature, stirring, increase in concentration of the supporting electrolytes and viscosity of the bath have been reported to favour dendritic growth [17]. The particle sizes of these samples range from 25 to 30 nm. The EDX spectrum taken on a single particle presented in Fig. 2e and f reveals the presence of both Ag and Fe. This is an evidence for the mixing of Ag and Fe atoms to form the alloy particles. The EDX spectrum indicates the presence of oxygen which is due to surface oxidation as commonly observed in nanosized particles. There is also a meagre amount of sulphur present on the surface which is likely to be from the complexing agent thiourea that gets adsorbed on the deposit just when the current is switched off before the removal of the substrate [18]. The TEM image of the sample 2B is depicted in Fig. 3. It

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