

Carbon-coated FeRu and CoRu nanomagnets

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ABSTRACT

This work presents a synthesis procedure for carbon-coated magnetic nanoparticles and the detailed characterization of the material regarding structure, morphology, and magnetic properties. To be specific, the high pressure chemical vapour deposition technique (HPCVD) has been applied to successfully produce carbon-coated nanoparticles with various magnetic core materials, such as FeRu, CoRu. The morphological and structural characterization of the materials has been done by means of transmission electron microscopy, energy dispersive X-ray spectroscopy and X-ray diffraction. A particular advantage of carbon-coated nanomagnets is oxidation protection of the magnetic core material which implies feasibility for biomedical applications. Here, the feasibility for magnetic hyperthermia therapies is exploited by investigating induced heating under applied alternating magnetic fields.

Keywords: Nanoalloys, HPCVD, Magnetism.

1 INTRODUCTION

The synthesis of metal nanoparticles of definite size and shape remains a challenging problem. This becomes even more difficult if bimetallic nanoparticles are concerned taking into account that in addition the composition must be controlled. However, recently alloy bimetallic nanoparticles have been extensively studied because they can exhibit unique electronic, optical, and catalytic properties that are absent in the corresponding monometallic nanoparticles. Furthermore, the addition of a second metal provides additional access to control the chemical and physical properties of nanoparticle. In addition to the magnetic nanomaterial, the shielding of the functional entities against the environment is a crucial issue. Hence, encapsulation of nanoparticles has been a major topic in the recent years, too, aiming at applications in such diverse fields as magnetic data storage, nanomedicine, electronics, magnetic resonance imaging (MRI), and so forth [1-9]. Beyond such applications, tailored synthesis of nanoscaled magnetic materials in complex core/shell structures as well as their physical properties are still relevant from a fundamental materials science point of view, in particular if the size effects on the the relevant parameters are concerned. The field of bimetallic and trimetallic nanoclusters

(nanoalloys) demonstrates the challenges and opportunities of this research field in a particular way. In nanoalloys, the chemical and physical properties may be tuned by varying the composition as well as the size of the clusters. They have already been used in various areas, ranging from catalysis (e.g., catalytic converters in automobiles and electrochemical fuel cells) to optoelectronic, magnetic, and even medical applications. In particular, the 4d transition metals such as Ru, Rh, and Pd, and the 3d transition metals such as Fe, Co, and Ni and their alloys have been addressed both in experimental and theoretical investigations. In this paper, for the first time we report on the synthesis of carbon-coated FeRu and CoRu nanoalloys (FeRu@C and CoRu@C) by means of the high-pressure chemical vapor deposition method (HPCVD) and we show the effect of the synthesis pressure on the materials properties such as the composition, the size, and the magnetic properties of these binary alloys.

2 MATERIALS AND METHODS

The high pressure chemical vapour deposition process (HPCVD) has been previously applied for the synthesis of carbon coated pure metals [10, 11]. For the synthesis of carbon coated FeRu and CoRu nanoalloys presented here, ferrocene, cobaltocene, nickelocene, and ruthenocene have been used as precursors for the nanoalloying constituents Fe, Co and Ru, respectively. Fe/Ru and Co/Ru metallocene powders, respectively, were mixed with a weight ratio of 2:1 and positioned in a separated crucible located in a thermostated chamber at 95 °C, and are sublimated and transported using argon gas flow (1400 sccm) into the CVD reactor (Fig. 1).

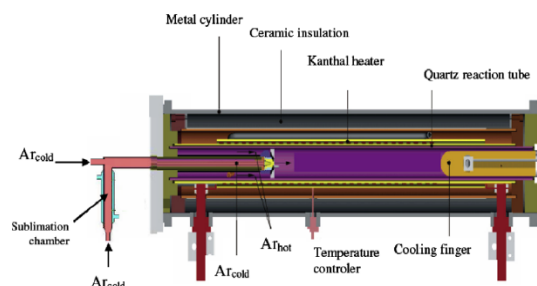


Fig. 1: Schematic diagram for HPCVD [10].

For all experiments the Ar flow rate was fixed at 1400 sccm while temperature (T) and pressure (P) inside the reactor were varied from 200 - 1000 °C and 5 - 40 bar, respectively. The optimal temperature for obtaining

spherical particles has been found to be $T = 900\text{ }^{\circ}\text{C}$ for the synthesis of both FeRu@C and CoRu@C. In order to synthesize different compositions of the nanoalloys, the pressure inside the reactor has been varied around the optimal value for spherical particles of XX for FeRu@C and XX for CoRu@C. As will be shown in detail below, the variation of the pressure affects the amount of Ru in the encapsulated alloy as well as the amount of carbon in the whole material. The materials have been characterized by several techniques. High-resolution transmission electron microscopy (HRTEM) was realized by means of a FEI Tecnai F 30 TEM with field emission gun at 300 kV. A FEI scanning electron microscope equipped with energy dispersive X-ray (EDX) analysis unit of EDAX has been used with a special program for determining the Ru-content inside the nanoalloy. A Miniflex X-ray diffractometer (XRD) with Cu K α radiation was used to identify the crystal structure. The magnetic field dependence of the magnetization at room temperature was measured by means of a MicroMag Model 2900 (Princeton Measurement Corp.) Alternating Gradient Magnetometer (AGM) [12].

3 RESULT AND DISCUSSION

3.1 Morphology and structure

The composition of the resulting material was investigated by EDX. In general, the synthesis process yields carbon coated FeRu and CoRu nanoalloys (FeRu@C, CoRu@C) with different compositions as listed in table 1 and 2 for FeRu@C and CoRu@C, respectively. For each batch, several EDX measurements were done at different positions of the sample in order to get average values for the core composition. As shown in table 1 and 2, the data imply that moderately increasing the synthesis pressure yields a higher Ru content in the produced FeRu and CoRu alloys. Also, the carbon contents in the material have been observed to be increased when the pressure have been increased.

Table 1: Composition of the FeRu@C nanostructures synthesized at different pressures as determined by EDX analysis.

Pressure (bar)	13	21	26
Ru (wt%)	17 ± 1	28 ± 2	41 ± 2
Fe _{100-x} Ru _x (x in wt%)	Fe ₈₃ Ru ₁₇	Fe ₇₂ Ru ₂₈	Fe ₅₉ Ru ₄₁
C (wt%)	18	30	57

Table 2: Composition of the CoRu@C nanostructures synthesized at different pressures as determined by EDX analysis.

Pressure (bar)	13	21	26
Ru (wt%)	31 ± 1	38 ± 3	39 ± 5
Co _{100-x} Ru _x (x in wt%)	Co ₆₉ Ru ₃₁	Co ₆₂ Ru ₃₈	Co ₆₁ Ru ₃₉
C (wt%)	22	34	40

The morphology of the coated particles was studied by HRTEM which confirms a nanostructured material exhibiting the core/shell structure Fig. 2. Typical examples of individual FeRu@C and CoRu@C particles are displayed in Fig. 2(b, e) which shows spherical FeRu and CoRu cores of about 26 and 23 nm, respectively, and a carbon shell of about 3 nm.

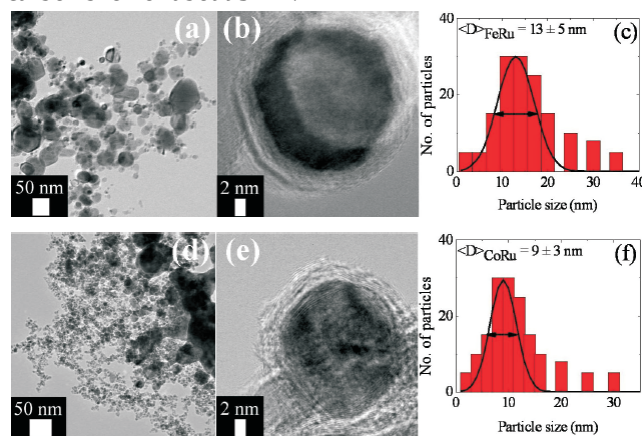


Fig. 2: HRTEM images and average size distribution of FeRu@C (a, b, c) and CoRu@C (d, e, f).

From the TEM studies, an average size of the FeRu and CoRu cores of $\langle D_{\text{TEM}} \rangle = 13 \pm 5$ and 9 ± 3 nm with a relatively large size distribution can be extracted as displayed in Fig. 2(c, f). The thickness of the carbon shells amounts to 2-3 nm. A typical XRD diffraction pattern of the deposited material is shown in Fig. 3. Noteworthy, characteristic peaks of other related compounds especially oxides have not been observed. The XRD results confirm the pure metallic constitution of the nanoalloys except for the case of FeRu, where the formation of Fe₃C is indicated by the peak at 50.1° . The diffraction peaks at $2\theta = (43.3^{\circ}, 44.3^{\circ})$ and $(40^{\circ}, 43.7^{\circ}, 46^{\circ}, 51^{\circ})$ are related to the main reflexes (002, 101) and (100, 111, 101, 200) of the FeRu and CoRu alloy, respectively. The very broad peak at $2\theta = 26^{\circ}$ is observed for all samples and corresponds to graphitic carbon shells and amorphous-like carbon. In addition, the XRD patterns allow to determine the average diameter of the nanoalloys cores by analyzing the width of the characteristic diffraction peaks (cf., e.g. [10]). Applying Scherrer formula yields average core diameters of 9 ± 2 (FeCo) and 6 ± 2 nm (CoRu) respectively, which agrees well with the TEM results.

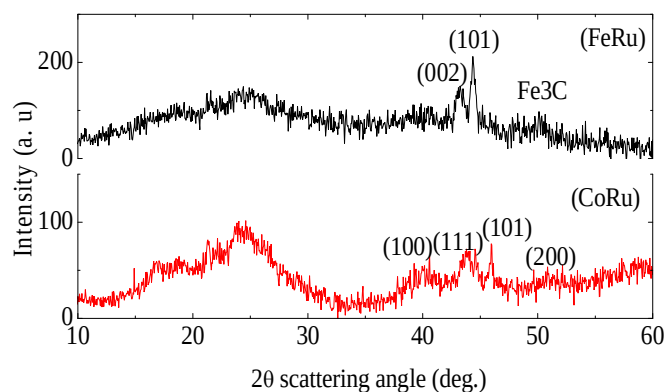


Fig. 3: X-ray diffraction spectra for FeRu@C and CoRu@C.

Note, that the width of the XRD peaks does not change significantly upon variation of the synthesis pressure, i.e. the mean diameters of the metallic cores do not significantly depend on the pressure. In contrast, the peak positions are slightly shifted which is in agreement with the observed changes in the composition of the nanoalloys.

3.2 Magnetic Properties

The magnetic properties of the prepared samples have been investigated by studies of the field dependence of the magnetization at room temperature as displayed in Fig. 4.

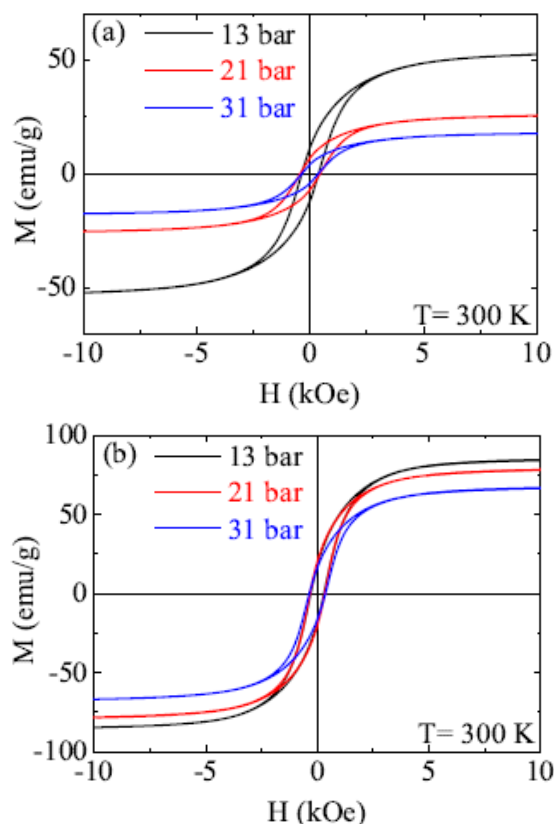


Fig. 4: Magnetization loops at room temperature of (a) FeRu@C (b) CoRu@C.

The data reveal a ferromagnetic behaviour at room temperature for all samples prepared at different pressure (open hysteresis loop). The quantitative analysis of the data reveals a clear dependence of the saturation magnetization M_s on the synthesis pressure as well as the composition of the alloy. In general, for the samples prepared at higher pressure, the C and the Ru content in the material increases and hence the magnetisation becomes smaller.

4 CONCLUSION

The synthesis of FeRu@C and CoRu@C nanoalloys using the HPCVD technique has been successfully demonstrated. The samples have been investigated with respect to their morphology and magnetic properties. Core/shell nanostructures of FeRu@C and CoRu@C have been confirmed by the analysis of the HRTEM and XRD data. X-ray diffraction studies reveal FeRu and CoRu binary alloys and no oxidized metals. It is to be particularly mentioned that the content of carbon in the deposited nanoalloy material clearly depends on the synthesis pressure while the average sizes of the nanoparticles do not significantly change. Hence, this allows to control the composition and hence the magnetic properties of the produced alloys by controlling the pressure during the synthesis process. The magnetization curves show ferromagnetic behaviour. Different values of the saturation magnetization are obtained which are affected by variations in the chemical composition of the alloy core but primarily are caused by different carbon contents in the deposited material, especially by more amorphous-like carbon while the thickness of the graphitic shells is relatively constant.

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