"Metallurgy" in a beaker: liquid phase synthesis and characterization of ferromagnetic FeNiCo-based nanoalloys

Garyfalia Nezou[1§], Alexandros Konstadinidis[1§], Georgia Basina[1], Vasileios Panagopoulos[1], Ioannis Panagiotopoulos[2] and Vasileios Tzitzios*[1]

[1] Institute of Nanoscience and Nanotechnology, National Centre for Scientific Research "Demokritos"

[2]Department of Materials Science and Engineering, University of Ioannina

*§ both authors are equally contributed * Corresponded author: v.tzitzios@inn.demokritos.gr*

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Abstract

FeCoNi-based nanoalloys were synthesized following a liquid phase approach. The effect of annealing, under reductive atmosphere, and the third element addition, on their properties were studied and the synthesized nanostructures were characterized by ***X-ray diffraction*** (XRD), ***Transmission Electron Microscopy*** (TEM), to estimate their structure and morphology, while the magnetic properties were studied using ***Vibrating Sample Magnetometry*** (VSM). The methodology is general and can be applied for the synthesis, in liquid phase, of a variety of nanoalloys at relative low temperatures.

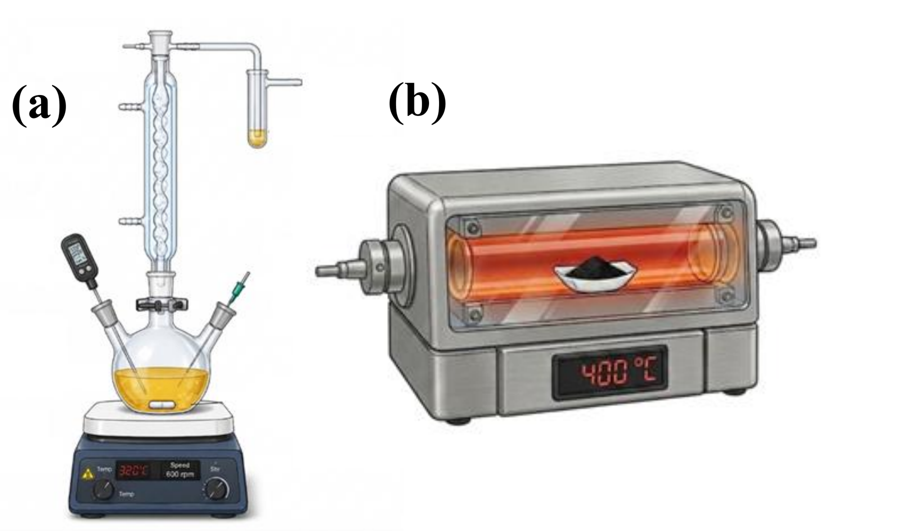
Introduction

Permanent magnets are vital in applications that range from home and office electronics to electric and hybrid vehicle motors and wind-turbine power generators. Modern high-performing permanent magnets rely on rare-earth-based intermetallics such as $Nd_2Fe_{14}B$ and $SmCo_5$.

Among a number of potential rare earth-free materials, nearly equiatomic ***ordered FeCo*** and ***FeNi*** alloys, have long been considered the "***holy grail***" in hard magnetism due to the abundance of their constituent elements and the remarkable magnetic characteristics supported by the anisotropic ***$L1_0$-type lattice***. Conventionally prepared nearly-equiatomic FeCo and FeNi alloys are, however, disordered: they crystallize in the *bcc* and *fcc* type structure correspondently and have negligible magnetocrystalline anisotropies.[1][2] In this case, because of the very low order-disorder transition, (~320°C for the case of FeNi), the thermally activated ordering is extremely slow, due to the very low atoms mobilities, and the times required to achieved would be astronomical. Therefore, there is a great need to develop methodologies for the synthesis of the FeCoNi-based alloys in ordered or anisotropic crystal structures.[5]

Here, we are developing liquid phase "metallurgical" synthetic methodologies following bottom-up approaches in order to affect atoms mobilities and enhance the formation of ordered or anisotropic structures. Our strategy based on the insertion of strains via the in-situ doping of the ferromagnetic nanoalloys.

Methodology



Scheme 1. (a) Schematic illustration of the experimental setup used for the synthesis of nanoparticles under H_2 atmosphere, consisting of a three-neck round-bottom flask equipped with a reflux condenser, thermocouple, and magnetic stirring/heating system *(b)* Schematic illustration of the tube furnace setup for the annealing experiments.

Briefly the synthesis of the *FeCoNi-based* nanoalloys was performed using the appropriate molar ratio of *Ni^{2+}, Co^{2+}, Fe^{2+} and Bi^{3+} inorganic salts e.g. acetylacetonates or acetates.* The metal salts were dissolved in a mixture of *oleylamine* and palmitic *acid, while 1-2 hexadecanediol was used* as reducing agent. The reactions were permormed under 6% H_2/Ar protective atmosphere at 320 °C for 1.5 hours. The particles were precipitated by ethanol and separated by centrifugation or by the use of a NdFeB laboratory magnet. Finally, the nanoalloys were annealed under H_2 (10% in Ar).

Results & Discussion

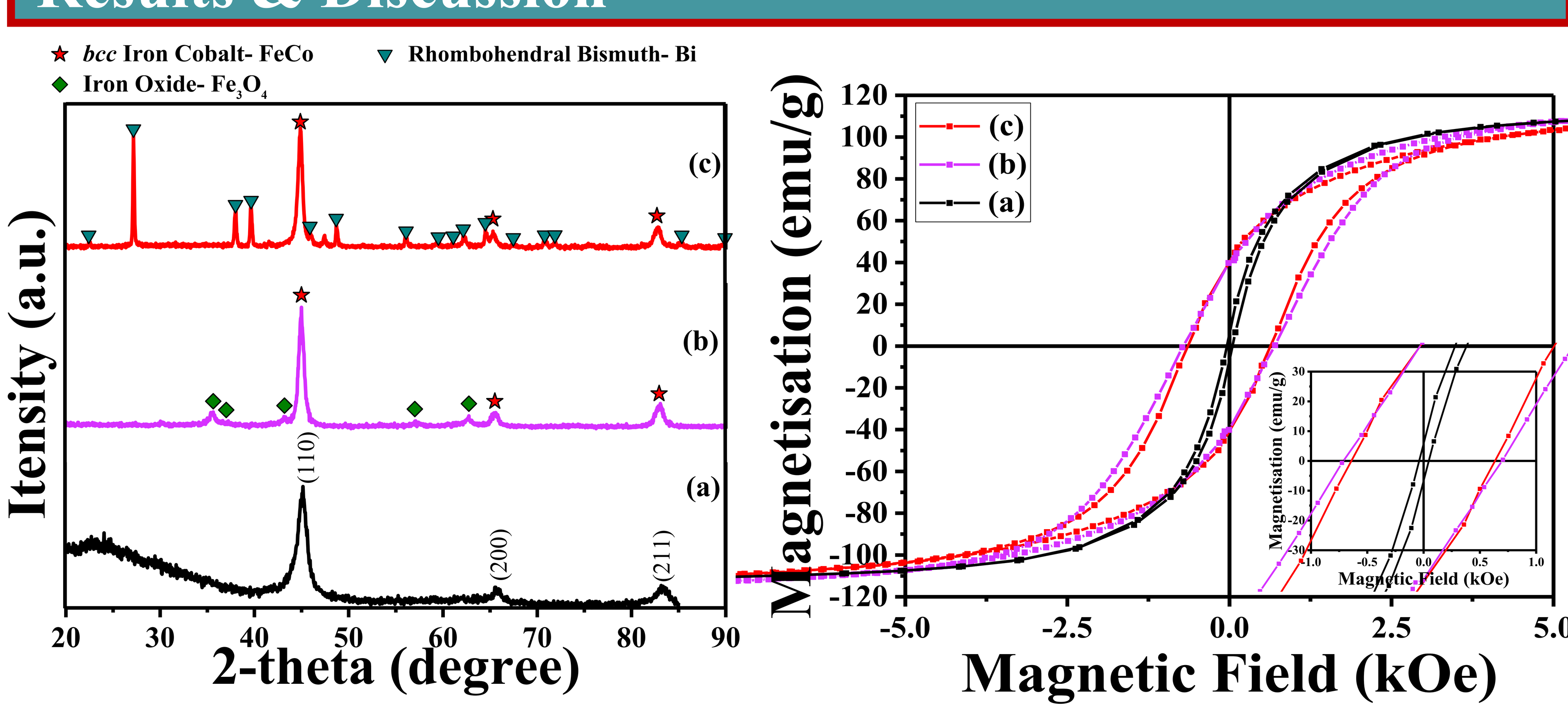


Figure 1. Powder X-ray diffraction patterns *(left)* and room temperature magnetic hysteresis loops *(right)* of equiatomic *bcc* FeCo (a) synthesized by the decomposition of $Fe(CO)_5$ and $Co_2(CO)_8$, (b) synthesized by polyol method annealed at 400°C/1h, (c) synthesized by polyol method with 5 at. % Bi annealed at 400°C/1 h.

X-ray diffraction patterns (Fig.1 left),confirmed that in all cases the FeCo alloys poses the *bcc* phase. However, the nanoalloys that were synthesized by the polyol approach, with or without the Bi addition, exhibit unconventionally high room temperature coercive fields, up to 710 Oe, for a cubic structured FeCo alloys (Fig.1b,c right). In contrast the metal carbonyls approach leads to formation of FeCo alloys that is exhibited low coercivity, (40 Oe), which is expected for similar materials (Fig.1a right). The unexpectedly high coercive fields may arise from strain introduced into the crystal lattice by the incorporation of the dopant species. Comparing the materials with and without bismuth doping we observe that there is no significant difference in the coercive fields which leads to the conclusion that the strains doesn't arising form the bismuth addition. Therefore, we assume that the enhanced coercive fields are probably due to the insertion of carbon atoms that are coming from the diol decomposition, which is capable of even leading to the synthesis of metal carbides[6], or by the exchange interactions with surface metal oxides, (left Fig.1b) which is not so likely because in the case of bismuth dopping there are no signs of metal oxides in the diffraction pattern (Fig.1c left).

Concerning the magnetization at 1.5 Tesla are 107, 114 and 112 emu/g, values that are in good agreement for FeCo nanoalloys in the nanosized regime.

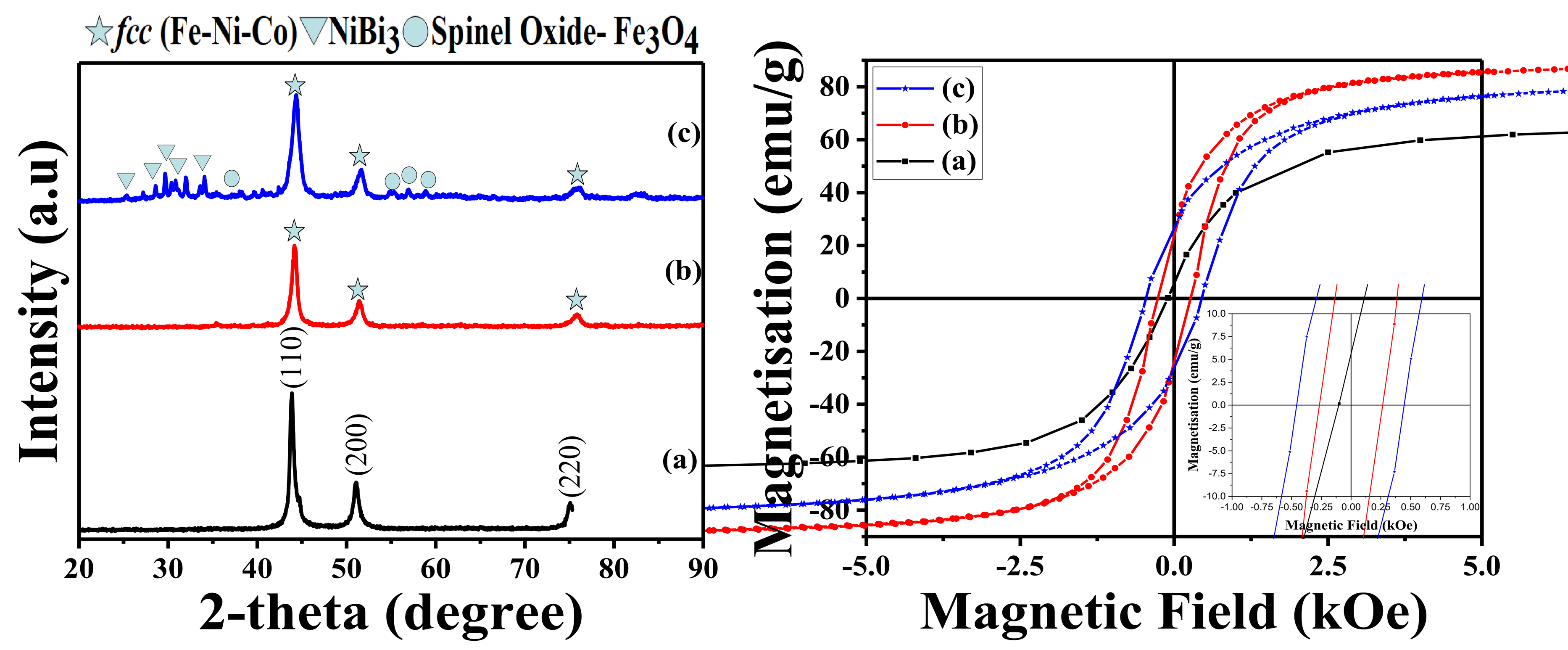


Figure 2. Powder X-ray diffraction patterns *(left)* and *r*oom temperature magnetic hysteresis loops *(right)* of $FeNi_{1-x}Co_x$ nanoalloys. With x=0 in the made form (a), x=0.1 annealed at 400°C, and (c) x=0.1 Bi doped annealed at 400°C (the compositions are nominal)

The powder XRD patterns of FeNi and cobalt-substituted FeNi nanoalloys confirm that the materials crystallize in the *fcc* structure, with mean particles diameter, estimated using Scherrer equation, that varied from 10.3 nm, in the as made form, to 12.8 nm after annealing at 400 °C. Additionally, in the case of Bi doping the $NiBi_3$ intermetallic and small amount of metal oxides Fe_3O_4 are also formed. The room temperature magnetic hysteresis loops shows that the partial substitution of nickel by cobalt increase both coercivity and magnetization from 105 Oe to 246 Oe and from 61.13 emu/g to 81.15 emu/g respectively, while the bismuth addition increase significantly the coercivity from 246 Oe to 507 Oe.

Figures 3 and 4 present the TEM images of the synthesized FeCoNi-based nanoparticles. Figure 3a shows equiatomic FeCo nanoparticles prepared via the carbonyl decomposition method, which are nearly monodisperse, spherical, and have an average diameter of ~8 nm. The crystallite size estimated using the Scherrer equation is ~7 nm. Figure 3b displays the equiatomic FeCo nanoparticles synthesized by the polyol method with 5 mol% Bi and annealed at 400 °C, which also exhibit a roughly spherical morphology but with a larger average particle diameter of ~15 nm and a crystallite size of ~17 nm. Similarly, the TEM images in Figure 4a reveal spherical particles, whereas after annealing (Fig. 4b) a dense aggregate is formed, with an average particle size of 12.8 nm. This value is in excellent agreement with the crystallite size calculated from the XRD patterns using the Scherrer equation. Overall, for all FeCoNi-based nanoalloys, the particle sizes determined from TEM analysis are consistent with the crystallite sizes, indicating that the nanoparticles are predominantly single-crystalline.

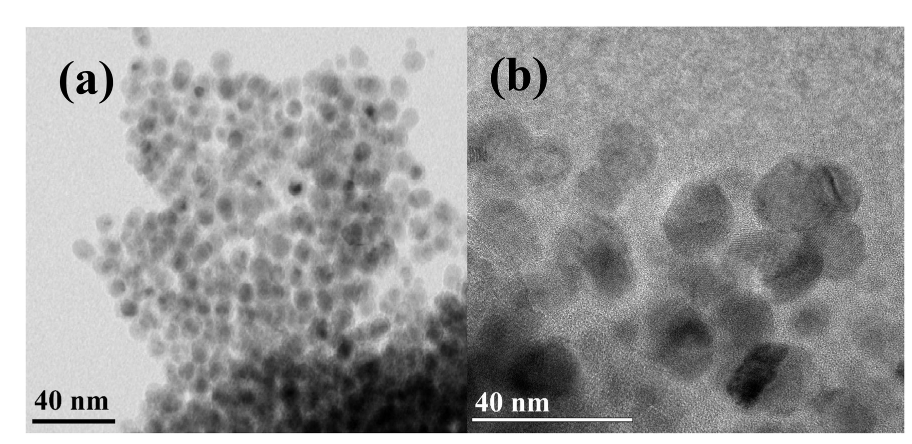


Figure 3. TEM images of FeCo nanoalloys: synthesized by carbolyl depomposition (a), and synthesized by the polyol method with 5% mol Bi annealed at 400°C (b).

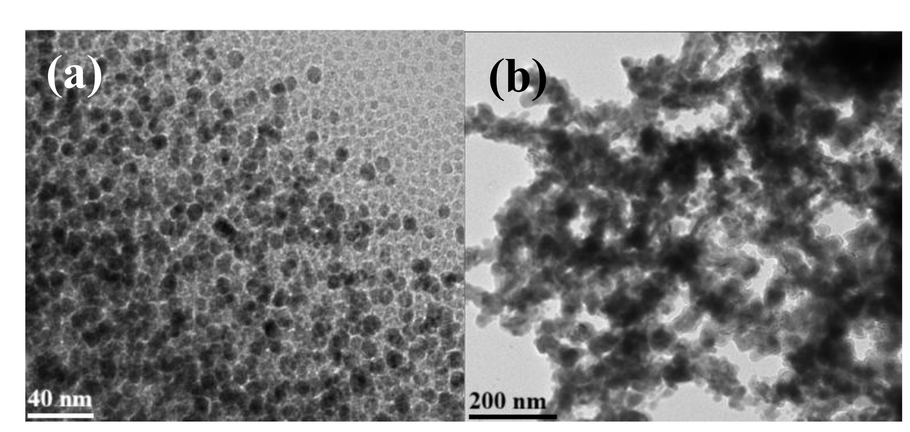


Figure 4. TEM images of bismuth doped $FeNi_{0.95}Co_{0.05}$ nanoalloys **in the** as- made (a), and annealed at 400°C form (b).

In Conclusion

In the FeCo-based alloys

- The bismuth addition it seems that does not contribute to the development of magnetic anisotropy, while its presence suppress the formation of metal oxides.
- The enhancement of the coercive field is most likely driven by carbon insertion, with additional contributions from exchange-interaction effects.

In the FeNi-based alloys

- The bismuth addition, as well as, the partial substitution of nickel by cobalt it seems that enhance the coercive field.

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References

[1] Jun Cui, Matthew Kramer, Lin Zhou, Fei Liu, Alexander Gabay, George Hadjipanayis, Balamurugan Balasubramanian, David Sellmyer, ***Current progress and future challenges in rare-earth-free permanent magnets*** (2018)

[2] Ihor Z. Hlova, Oleksandr Dolotko, Mykola Abramchuk, Anis Biswas, Yaroslav Mudryk, Vitalij K. Pechars ***Enhancement of hard magnetism and chemical order of synthetic $L1_0$-FeNi*** (2024)

[3] V. Tzitzios, G. Basina, D. Niarchos, Wanfeng Li and G. Hadjipanayis, ***Synthesis of air stable FeCo nanoparticles*** (2011)

[4] Frank M. Abel, Vasileios Tzitzios, Eamonn Devlin, Saeed Alhassan, David J. Sellmyer and George C. Hadjipanayis, ***Enhancing the Ordering and Coercivity of $L1_0$ FePt Nanostructures with Bismuth Additives for Applications Ranging from Permanent Magnets to Catalysts*** (2019)

[5] Aldo Capobianchi, Marcello Colapietro, Dino Fiorani, Sabrina Foglia, Patrizia Imperatori, Sara Laureti and Elia Palange, ***General Strategy for Direct Synthesis of $L1_0$ Nanoparticle Alloys from Layered Precursor: The Case of FePt*** (2009)

[6] Frank M. Abel, Shirin Pourmiri, Georgia Basina, Vasileios Tzitzios, Eamonn Devlinc, George C. Hadjipanayis, ***Iron carbide nanoplatelets: colloidal synthesis andcharacterization*** (2019)