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DISCLAIMER

ABSTRACT

Nanostructured magnetite/T multilayers, with T = Ni, Co, Cr, have been prepared by pulsed laser deposition. The thickness of individual magnetite and metal layers takes values in the range of 5 - 40 nm with a total multilayer thickness of 100 -120 nm. X-ray diffraction has been used to study the phase characteristics as a function of thermal treatment up to 550 ºC. Small amounts of maghemite and hematite were identified together with prevailing magnetite phase after treatments at different temperatures. The mean grain size of magnetite phase increases with temperature from 12 nm at room temperature to 54 nm at 550 ºC. The thermal behavior of magnetite in multilayers in comparison with powder magnetite is discussed. These findings were published in peer-reviewed conference proceedings after presentation at an international materials conference.

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INTRODUCTION

In the last decade the study of magnetic thin films and multilayers has received considerable attention due to the possible applications in planar devices and high density recording [1-3]. In particular, magnetite multilayers are of great importance since the construction of a magnetite-based all-oxide spin valve was anticipated [4]. In the last few years, pulsed laser deposition (PLD) became a powerful method for preparing magnetic thin films and multilayers [5-7].

It is the aim of this paper to report on the preparation of magnetite/nickel, magnetite/cobalt and magnetite/chromium multilayers by PLD and to present the results of the X-ray diffraction (XRD) studies on the samples after annealing at different temperatures up to 550°C. Generally, polycrystalline magnetite is quickly oxidized to maghemite (γ-Fe_2O_3) in air [8]. Magnetite crystals smaller than ~ 300 nm transform to maghemite at 200 to 250°C, which in turn transform to hematite (α-Fe_2O_3) above 500°C. If the magnetite particles are larger than 300 nm, hematite nuclei formed at lower temperatures can bypass the formation of maghemite. For temperatures greater than 500°C, magnetite changes directly to hematite. In this report the thermal behavior of magnetite in multilayers is analyzed in comparison with powder magnetite.

EXECUTIVE SUMMARY

This project proposes and achieves the laser ablation deposition of Fe_3O_4/T multilayers, with T=Ni, Cr and Co. The total thickness of the multilayers was about 100 nm, with individual layer thickness in the range 5-40 nm. The multilayers were subjected to postdeposition annealing at temperatures up to 550^{o}C. We used X-ray diffraction in order to characterize the phase characteristics as a function of thermal treatment. The average grain size of magnetite phase was found to increase from 12 nm at room temperature to 54 nm at 550^{o}C. Finally, we provide a direct comparison between the thermal behavior of magnetite in multilayers and that of bulk magnetite.

EXPERIMENTAL

A Lambda Physik COMPEX 102 excimer laser working at a wavelength of 248 nm and a pulse width at half maximum of 8 ns was used to perform the pulsed laser deposition. The laser pulse energy was 450 mJ at a repetition rate of 10 Hz. For all samples the deposition was performed on Si (111) substrates using iron, nickel, cobalt and chromium targets in an oxidizing atmosphere. The multilayers obtained were magnetite/nickel, magnetite/cobalt and magnetite/chromium, with a total thickness of 100-120 nm. They were of the type: $[Fe_3O_4/T]_{10}$, $[Fe_3O_4/T]_5$, $Fe_3O_4/T/Fe_3O_4/T/Fe_3O_4$ and $Fe_3O_4/T/Fe_3O_4$ where the transition element T = Ni, Co and Cr. The magnetite and metal layer thicknesses had the values 5, 10, 20 and 40 nm. The as-obtained multilayers were analyzed by standard X-ray diffraction using a Rigaku D-2013 diffractometer with Cu K_α radiation, at room temperature. The thermal treatments (Rapid temperature furnace, Bloomfield N. J.) were performed in ambient atmosphere, for 6 hours, at 250°C and 550°C. After each annealing the samples were cooled down to room temperature and investigated by XRD.

RESULTS AND DISCUSSION

XRD spectra of as-obtained multilayers reveal the crystallization of Fe_3O_4 (magnetite) phase. Not all the characteristic lines (see the JCPSD data, card no.19-0629) are present in the recorded XRD spectra, indicating preferential crystallographic growth directions of the structure on the layer surface. The most representative lines are (220) and (440) as can be seen for the case of an $[Fe_3O_4/Ni]_{10}$ multilayer in Figure 1.

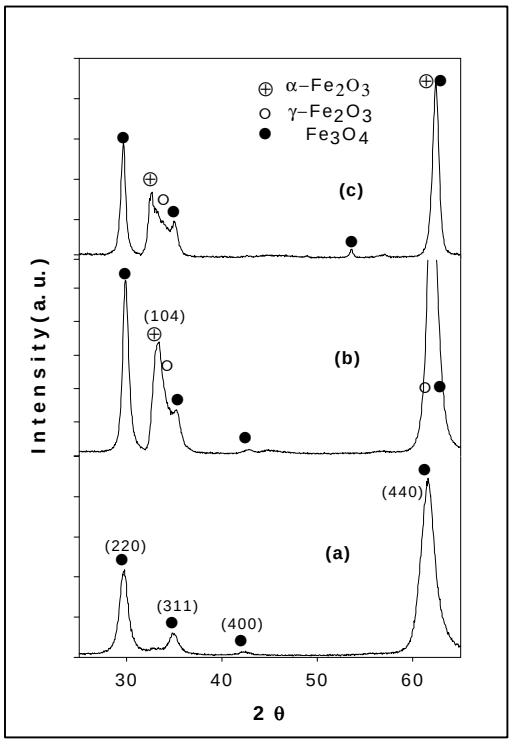

Figure 1.

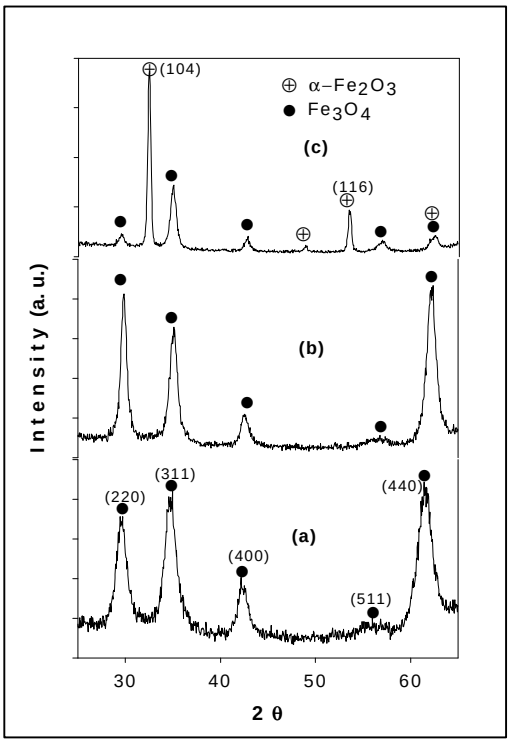

Figure 2.

The magnetite structure was confirmed also by conversion electron Mössbauer spectroscopy (CEMS) investigations [9]. The thermal behavior of the multilayers depends on the transition element layer T as well as on the multilayer design. One can infer from Figure 1 the appearance of γ-Fe_2O_3 and α-Fe_2O_3 at 250 °C, but the Fe_3O_4 phase is still present. This behavior is different from the case of powder magnetite as discussed previously. A particular behavior can

be seen in Figure 2 (a-c) where the XRD spectra of Fe_3O_4/Ni/Fe_3O_4/Ni/Fe_3O_4 are displayed. The magnetite phase remains also at 250°C and no maghemite phase can be identified in contrast to the powder case. Narrower lines at higher temperatures are associated with an increase in grain size dimension from 12 nm to 21 nm (see Table I). The values obtained for the mean diameter are consistent with bidimensional growth in this system.

In the case of the $[Fe_3O_4/Co]_5$ multilayer (Figure 3) the nanostructured magnetite is a rather stable phase. At 250°C one can observe a maghemite phase that disappears at 550 °C where only the magnetite phase remains. The main effect of the thermal treatment in this case is the increase in the magnetite grain size from 14 to 32 nm (Table I). A different behavior can be observed in the as-obtained Fe_3O_4/Co/Fe_3O_4 multilayer where some lines of hematite and maghemite are already present (Figure 4a).

Table I. Particle mean dimension of the magnetite phase in some investigated multilayers, as given by Scherrer equation. All thermal treatments were performed in ambient atmosphere, for 6 hours.

Sample	Thermal treatment (ºC)	Layer thickness (nm)	Mean dimension (nm)
$[Fe_3O_4/Ni]_{10}$	RT		15
	250	5	25
	550		32
$[Fe_3O_4/Co]_5$	RT		14
	250	10	22
	550		32
$Fe_3O_4/Ni/Fe_3O_4/Ni/Fe_3O_4$	RT		12
	250	20	21
	550		30
$Fe_3O_4/Co/Fe_3O_4$	RT		14
	250	40	18
	550		31
$Fe_3O_4/Cr/Fe_3O_4$	RT		14
	250	40	23
	550		54
Error	± 1.5	± 2	± 1.5

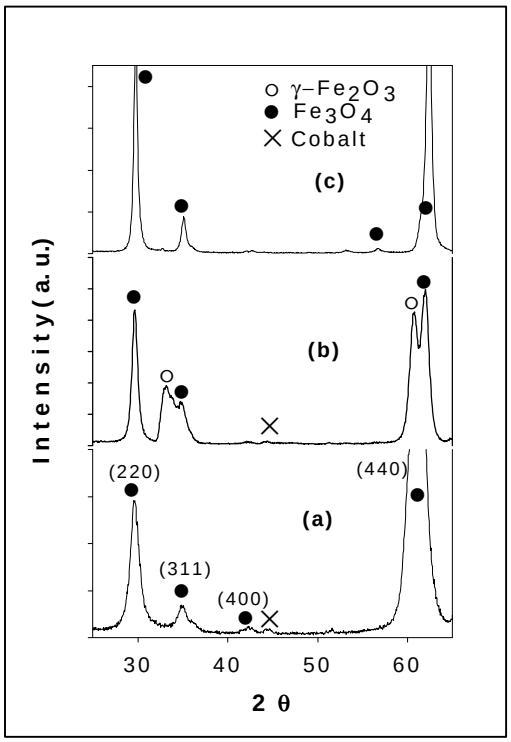

Figure 3.

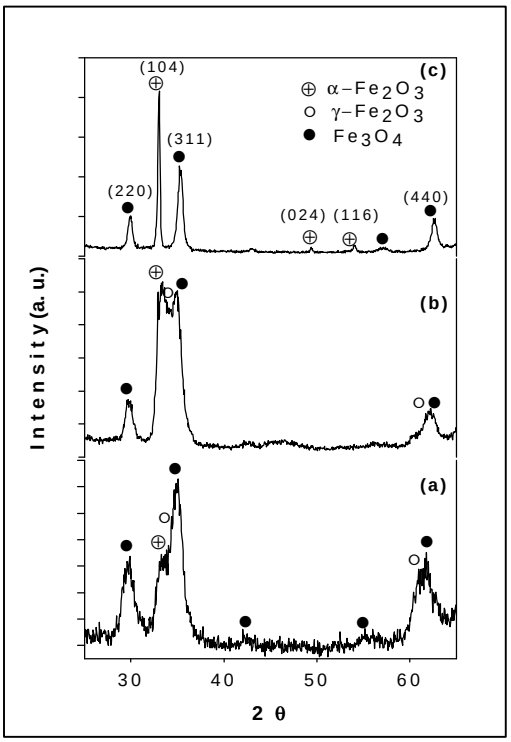

Figure 4.

The hematite lines (104) and (116) can be seen together with magnetite lines at 550°C. The maghemite phase can be recognized at 250°C but at 550°C only magnetite and hematite lines are present in the XRD spectrum.

In the XRD spectra of $Fe_3O_4/Cr/Fe_3O_4$ represented in Figure 5, a small line that belongs to hematite can be seen in the as-obtained multilayer together with the magnetite phase.

The hematite phase increases with temperature and is the dominant phase at 550°C (Fig. 5c). No maghemite phase is observed in the analyzed $Fe_3O_4/Cr/Fe_3O_4$ multilayer.

For all investigated multilayers, the longer thermal treatments at 550°C have not changed the phase distribution. Table I shows the increase of particle dimension as the temperature increases in all cases but the magnetite phase remains nanostructured. The particle dimensions were determined from XRD lines using the Scherrer equation [10]. The full-width-at-half-maximum

requested by the Scherrer equation has been obtained by the computer fit of the XRD spectra. The best fit was given by the Lorentzian line shape approximation. We have to mention that Scherrer formula measures the domain size and therefore underestimates the true crystal size of multidomain crystals. Moreover, the formula does not consider the contribution of the structural strain to the line broadening.

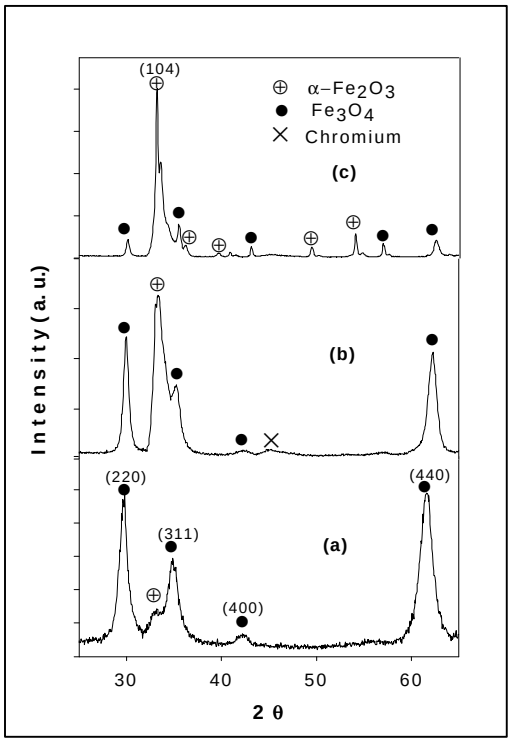

Figure 5.

CONCLUSIONS

We have prepared nanostructured magnetite/T multilayers of the type $[Fe_3O_4/T]_{10}$, $[Fe_3O_4/T]_5$, $Fe_3O_4/T/Fe_3O_4/T/Fe_3O_4$ and $Fe_3O_4/T/Fe_3O_4$ where the transition element T = Ni, Co and Cr, by pulsed laser deposition. XRD analysis shows that in contrast to the case of powdered material, in our multilayers the magnetite is still present at 550°C, generally accompanied by small amounts of hematite. The most temperature stable multilayer configurations are $Fe_3O_4/Ni/Fe_3O_4/Ni/Fe_3O_4$ (up to 250°C) and $[Fe_3O_4/Co]_5$ which at 550°C exhibit only the magnetite phase. Further studies regarding the structural and magnetic properties of these multilayers are in progress.

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LIST OF ACRONYMS AND ABBREVIATIONS

XRD=X-ray diffraction

PLD=Pulsed Laser Deposition

LIST OF PUBLICATIONS

1. **M. Sorescu**, A. Grabias and L. Diamandescu, "Magnetite/Nickel and Magnetite/Cobalt Multilayer Nanostructures Obtained by Pulsed Laser Deposition", in: "Nanostructured Materials with Energetic Beams", edited by A. Meldrum, S. Roorda and H. Bernas, **Materials Research Society Symposium Proceedings**, 777 (2003) 59-65.

Since the last report the following papers were published or accepted for publication:

1) **M. Sorescu** and M. Valeanu, "Effect of Substitutions on the Hyperfine Magnetic Field in Nd-Based Intermetallics", **Intermetallics** 11 (2003) 749-754.

2) **M. Sorescu**, A. Grabias and M. Valeanu, "A Mössbauer Study of Spring Magnets", **IEEE Transaction on Magnetics** 39 (2003) 2959-2961.

3) **M. Sorescu**, F. Pourarian and R.A. Brand, "Mossbauer Study of Hydrogenation Effects in Iron-Rich Intermetallics", **Journal of Materials Science Letters**, in press.