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To cite this version:
P. Camus, R. Shull, A. Melmed. APFIM ANALYSIS OF COMPOSITE MAGNETIC THIN FILMS. Journal de Physique Colloques, 1989, 50 (C8), pp.C8-343-C8-347. <10.1051/jphyscol:1989858>. <jpa-00229956>

HAL Id: jpa-00229956
https://hal.archives-ouvertes.fr/jpa-00229956
Submitted on 1 Jan 1989

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APFIM ANALYSIS OF COMPOSITE MAGNETIC THIN FILMS

P.P. CAMUS*, R.D. SHULL** and A.J. MELMED***

*National Institute of Standards and Technology, Gaithersburg, MD 20899, U.S.A.
**Surface Science Division, Gaithersburg, MD 20899, U.S.A.
***Metallurgy Division, Gaithersburg, MD 20899, U.S.A.
****Custom Probes Unlimited, PO. Box 3938, Gaithersburg, MD 20878, U.S.A.

Abstract - Composite thin films prepared by sputter co-deposition of Fe₃O₄ with small additions of Ag were investigated in this feasibility study. These nanocomposites possess unique magnetic properties which may be controlled by compositional variations. Atom probe field-ion microscopy was used to investigate the microstructure and microchemistry of the material. Field-ion microscopy in hydrogen was found to be the most suitable method to provide microstructural contrast. Atom probe analysis using electrical pulses at various temperatures proved to be feasible and indicated that the Ag is not homogeneously distributed. Even though the bulk of this material (Fe₃O₄) is regarded as having a low electrical conductivity, there obviously must exist enough conductivity for APFIM and this indicates that imaging and analysis of other low conductivity materials may not be as improbable as once seemed.

INTRODUCTION

Unique morphologies and physical properties often occur when two immiscible materials, usually a metal and a non-metal, are co-deposited from the vapor phase to form a thin film.(1,2) A polycrystalline composite structure consisting of nearly pure grains of each material is usually observed having a granular size of the order of a few nanometers. If the metallic species is ferromagnetic, the magnetic properties of the composite strongly depend upon the volume fraction of the magnetic phase.(3-5) The same general behavior has also been observed for a ferromagnetic non-metal (Fe₃O₄) combined with a non-magnetic metal(Ag).(6) Mossbauer effect data have shown a change in the magnetic properties as a function of Ag content and test temperature. Electron diffraction confirmed the presence of two phases consisting of Ag and Fe₃O₄; however, compositional analysis (30 nm resolution) was unable to resolve these regions. It was presumed that the addition of silver could be modifying the size or distribution of the magnetic iron-oxide grains, although the distribution of the silver was not known.

Therefore, atom probe field-ion microscopy (APFIM) was attempted to investigate the microstructure and microchemistry of this nanocomposite thin film material. Successful AP mass analysis using an electrically pulsed conventional AP was not a priori obvious. The Ag content of the materials of the greatest interest from a magnetic properties standpoint was typically < 25%. Thus, the electrical properties of the composite could be expected to be dominated by the major Fe₃O₄ phase (although modified by the Ag addition), which has a low electrical conductivity at room temperature and an even lower conductivity at 85K.(6)

EXPERIMENTAL

Thin films of Ag and Fe₃O₄ were prepared by rf diode sputtering from a mechanical mixture of high purity Ag and Fe₃O₄ powders onto a fused silica substrate.(7) Typical specimen thicknesses were 1-2µm after sputtering for 7 h, Fig. 1. The composition of the thin films was not the same as that of the target material, but was determined quantitatively by energy dispersive x-ray analysis (EDX) in a scanning electron microscope and calculated to be (assuming all the Fe is bound as Fe₃O₄, as per the electron diffraction results) 4 at. % Ag - 96 at. % Fe₃O₄, i.e. 4 % Ag - 41 % Fe - 55 % O.

Because conventional TEM specimen preparation techniques of electropolishing and ion milling created uncontrolled artifacts,(7) and because of the thin form of the material, specimens for APFIM were prepared using the fracturing method of sharp pointed shards.(8) The thin film was tapped with a solid metal knife handle, and sharply pointed shards, Fig. 2, were conductively epoxied to tungsten points. Field-ion microscopy was performed at ~65K using 10⁻³ Pa of H₂ and N₂+H₂ gases, while atom probe analyses were performed typically at ~85K in <10⁻⁶ Pa vacuum.
RESULTS

Hydrogen was the first imaging gas used and the resultant field-ion images did not show much structure, but showed some very bright and very dark regions within a dim matrix, Fig. 3. The bright regions seemed to grow, then shrink and disappear with field evaporation indicative of isolated particles in a matrix. Some of the particles were large enough to give an indication of a ring structure. Nitrogen was then added to the imaging mixture which gave rise to the appearance of many more matrix atoms in the image, thus filling in the field of view. It then became apparent that the extremely darkly imaging regions were not matrix material but persisted after extended field evaporation, giving the impression that these features were voids. This result may be expected due to the sample fabrication by a sputtering technique.

Atom probe analysis of the material with liquid nitrogen cooling was possible with electrically pulsed field evaporation, and identifiable peaks could be obtained, Fig. 4. A slight difficulty arose in the interpretation of the spectra due to the close proximity of certain Ag and Fe peaks. Because the Ag concentration is low, the amplitude of any set of isotopic peaks is low and identification is somewhat difficult. An interesting feature of the spectra is the dominance of the peak at m/z=19. Possibilities for the assignment of this peak that must be considered are (1) Ne+, (2) Ar+2, (3) H₂O⁺, and (4) Fe⁺++. The assignment of this peak to either of the noble gases was discounted because the mass value of the peak was much lower than expected (m/z=20). If the rest of the spectrum was calibrated to force this peak assignment, other assignment problems would then develop at higher masses. The assignment to a H₂O⁺ peak is possible, as it fits rather well with the 15, 16, 17, and 18 peaks that are also observed in the spectrum. However, for both metallic (high evaporation field) and high temperature superconductor (lower evaporation field) specimens in the same system (under approximately the same vacuum conditions), the m/z=18 and 19 peaks are always very small, much smaller than the 16 and 17 peaks. This observation tends to disavow this assignment as H₂O⁺. The assignment to Fe⁺++ fits very well to the expected mass value (m/z=18.7). It should be noted if this peaks is assigned to H₂O⁺ (either from the material or the vapor phase), then the Fe content would be very much smaller than the expected value. This could be expected if the tip fractured and only gas was detected, however, the tip was still good after the analysis (tip voltage only changed a few kV to 10 kV max). Therefore, the only assignment that we feel comfortable in making for the peak at m/z=19 is Fe⁺++. There is no obvious reason for the appearance of this charge state and no speculation will be given except to note that this observation implies that a higher-than-normally-expected field was applied to the specimen.

Using the peak assignments in Fig. 4, the average composition of the material was determined to be 2%Ag - 35%Fe - 63%O which is in reasonable agreement with the values determined by EDX. The shape of a composition profile through the material, Fig. 5, is of more interest. The profile shows regions that possess Ag concentrations as high as 5% while other regions have concentrations as low as 0.5%. The Fe-O ratio was also observed to be larger for the Ag-enriched regions than for the Ag-depleted regions. The average size of the enriched region could only be estimated as ≈25nm, which is similar in size to the particle diameters predicted by the Mossbauer results.(7)

To permit easier field evaporation, analyses were attempted at higher specimen temperatures by cooling the specimen with dry ice and acetone (≈217K, ≈-56°C). This facilitated a rapid collection rate with a larger likelihood of survival of the specimen. However, field evaporation then produced mainly large-mass ionic clusters, which made peak identification difficult, Fig. 6. Because of the difficulties involved, this technique was not employed for composition determination, but indicates that slightly higher specimen temperatures may increase the electrical conductivity(6) and promote easier evaporation.

CONCLUSIONS

Specimens of a Ag-Fe₃O₄ thin film nanocomposite produced stable images in a field-ion microscope and compositional analyses were performed with an electrically pulsed AP in spite of the initial presumption of low electrical conductivity. There obviously must exist enough conductivity for APFIM and this indicates that imaging and analysis of other low conductivity materials may not be a improbable as once seemed. AP composition profiles indicate that the material is not homogenous with respect to the Ag content, but that the Ag cluster size is similar to that predicted earlier. Work is continuing to quantify the size and amplitude of the Ag fluctuations.
REFERENCES

Figure 1. Optical micrograph of thin film nanocomposite of Ag-Fe₃O₄ on silica substrate. The dark band on the circular glass slide is the film, whose thickness is approximately 1-2μm.

Figure 2. Optical micrograph of sharp pointed shards of Ag-Fe₃O₄ thin film. The fragment marked in the figure was epoxied to a tungsten point and analyzed in the APFIM.
Figure 3. H₂ field-ion micrograph of an Ag-Fe₃O₄ specimen obtained at 85K and =10kV. Arrows indicate brightly imaging clusters.

Figure 4. Atom probe mass spectrum of Ag-Fe₃O₄ obtained at 85K.
Figure 5. AP composition profile through an Ag-Fe₂O₃ specimen. The figure indicates that the Ag is not homogeneously distributed but there are regions enriched and depleted in Ag.

Figure 6. Atom probe mass spectrum of an Ag-Fe₂O₃ specimen obtained at =217K, =-56°C. Peak identifications are difficult due to large mass ionic cluster formation.