IN SITU TEM OBSERVATION OF NUCLEATION AND GROWTH OF Co NANOPARTICLES IN ZIRCONIA MATRIX

M. García del Muro, Z. Konstantinović, X. Batlle and A. Labarta
Dpt. de Física Fonamental i Institut de Nanociència i Nanotecnologia, Universitat de Barcelona, Martí i Franquès 1, 08020-Barcelona, Spain
montse@ffn.ub.es

Granular films of Co nanoparticles embedded in a zirconia matrix were prepared by KrF pulsed laser deposition (PLD). Zirconia was stabilized with 7 mol.% Y_2O_3, which provides the matrix with very good properties, such as good oxidation resistance, thermal expansion coefficient matching that of metal alloys and very high fracture toughness values. It has been observed that ZrO_2 matrix gives rise to sharper interfaces between the amorphous matrix and nanoparticles [1]. Besides, the high oxygen affinity of ZrO_2 prevents oxidation of the metallic nanoparticles. The samples were deposited at room temperature in a vacuum chamber with rotating composite targets made of sectors of ZrO_2 and pure cobalt. The distance between target and substrate was fixed at 30 mm. The laser fluency was typically 3 Jcm^{-2} . Average compositions were determined by microprobe analyses. The substrates for TEM experiments were silicon nitride membrane windows enabling direct observation of as-deposited samples.

We have previously shown [2] that for Co volume concentration $x < 0.31$, the particles have mostly spherical shape, while for $x \geq 0.31$, the neighboring particles start to coalesce, giving rise to larger, non spherical shape, indicating the rapid approach to the percolation threshold. About x=0.35, the size distribution broadens abruptly because of the massive coalescence of the nanoparticles that leads to percolation. In the present work, and in order to directly obtain infromation about particle growth mechanisms, we have performed TEM observations using a Hitachi 800MT electronic microscope equipped with a heating specimen holder. The selected samples are in the region $0.25<x<0.31$, so below the Co concentrations at which coalescence starts to be significant. The heating rate was about 50 ^{o}C/min from room temperature to 300 ^{o}C. TEM images were obtained after 15 min waiting for stabilization of both temperature and microscope electronics. Then whe increased the heater power to reach 400 ^{o}C and waited again before obtaining new images.

Figure 1 shows TEM images of practically the same area of Co-ZrO_2 film before and during in situ heating at 300 ^{o}C. Comparing the two images we can observe, at a glance, a significant and new fact: the number of small particles has increased. Particle size distribution extracted from TEM images shows, on one hand, the appearance of small particles with annealing, and on the other hand, that the mean size of the particles slightly increases with annealing. After annealing at 400 ^{o}C, a bimodal particle size distribution has to be assumed to fit experimental data, demonstrating both effects of annealing: nucleation of new particles from Co atoms dispersed in the zirconia matrix, and growing of the previously existing particles by adhesion of neighbour atoms and by coalescence. Previous similar works have only shown the second effect (see for example [3]).

Magnetic characterization by measuring the temperature dependence of the magnetization after field cooling and zero-field cooling the samples was done with the as-prepared samples and after annealings at 300 ^{o}C and 400 ^{o}C. The experimental results are fitted assuming particle size distributions which confirm the observed by direct TEM imaging.

References:

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[2] Z. Konstantinović, M. García del Muro, M. Kovylina, X. Batlle and A. Labarta, Phys. Rev. B, **79** (2009) 094201.
[3] G. Palasantzas, T. Vystavel, S.A. Koch and J.Th.M. De Hosson, J. of Appl. Phys., **99** (2006) 024307.

Figures:

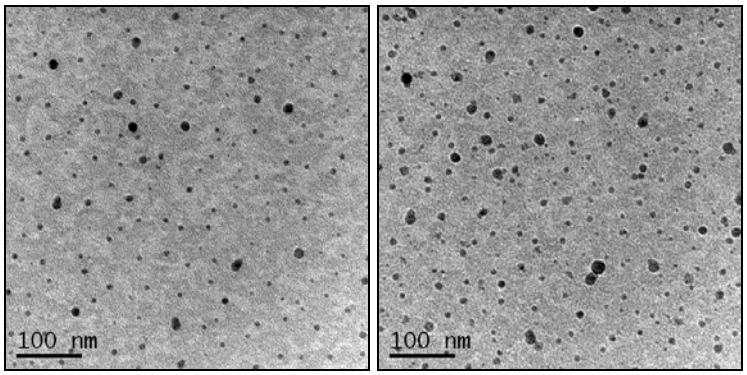

Figure 1. Bright field TEM images of the same area of Co-ZrO_2 film before (left) and during heating (right) at 300 ^{o}C.