Annex 3

Morphological and Structural Characterization

In this chapter the morphological and structural properties of FM particles (Co or $SmCo_5$), ball milled alone and together with AFM (NiO or CoO) powders are analyzed. The similarities and differences between the different systems are examined. The role of microstructure on the magnetic properties of the milled powders will be discussed in annexes 4 and 5.

3.1.- Morphological Characterization

3.1.1.- The morphology of unmilled and as-milled ferromagnetic particles

Morphological characterization of Co and $SmCo_5$ powders was carried out by means of scanning electron microscopy (SEM) [1-6]. The observations were performed mainly in particles embedded in epoxy resin and subsequently polished with diamond paste and alumina. However, Co powders were also observed after simply depositing them on the SEM holder, which allows to obtain 3-dimensional images of the particles.

SEM observations reveal that the starting Co particles have rounded shapes and sizes up to 40 μm. Since they are metallic and ductile, when they are ball milled alone, they become progressively elongated, turning into small platelet-shaped particles of a few μm in size. For example, shown in figure 3.1 are the SEM images (obtained from secondary electrons) of Co particles, before milling (a) and after milling for 20 h (b). It is noteworthy that the Co particles tend to elongate already during the first stages of the milling process and no significant morphological differences are observed for longer milling times.

Figure 3.2 shows the morphological evolution of $SmCo_5$ particles when subjected to the ball milling process. These images were obtained after embedding the powders in epoxy resin and polishing with diamond paste. As can be seen in figure 3.2 (a), the starting $SmCo_5$ particles have more irregular shapes, e.g. many of them have some sharp corners. Furthermore, they are more irregular in size than the unmilled Co powders. Some of the unmilled $SmCo_5$ particles have sizes of up to 500 μm.

(a)

(b)

Figure 3.1: SEM images (secondary electrons) of Co particles before milling and after milling for 20 h.

As the milling proceeds, $SmCo_5$ particles are progressively reduced in size and homogenized in shape. For example, as can be seen in figure 3.2 (b), after milling for 32 h, the majority of particles have sizes of less than 10 μm and a smoother shape.

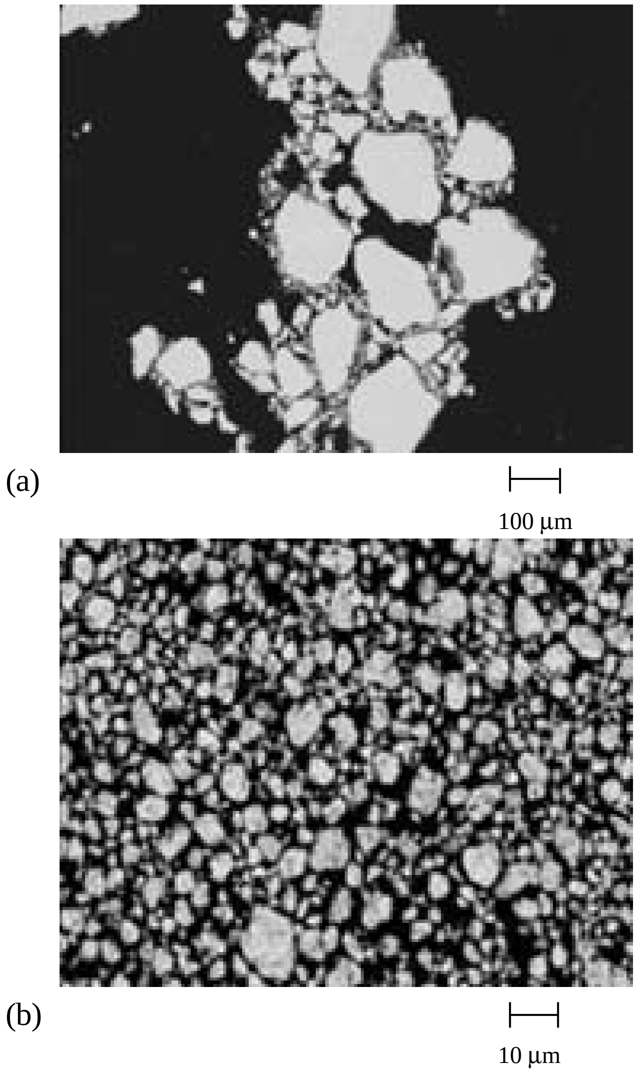

Figure 3.2: SEM images (backscattered electrons) of $SmCo_5$ particles before milling (a) and after milling for 32 h (b).

3.1.2.- Morphology of ferromagnetic-antiferromagnetic composites

When the FM particles are ball milled with NiO a different microstructure is encountered. The SEM images (backscattered electrons) of Co-NiO ball milled in the 1:1 weight ratio for 0.1, 1 and 20 h are displayed in figure 3.3. It can be seen that after milling for 0.1 h, Co and NiO powders are well mixed but still remain independent, i.e. not soldered together. Therefore, the amount of interfaces between Co and NiO for short milling times is small.

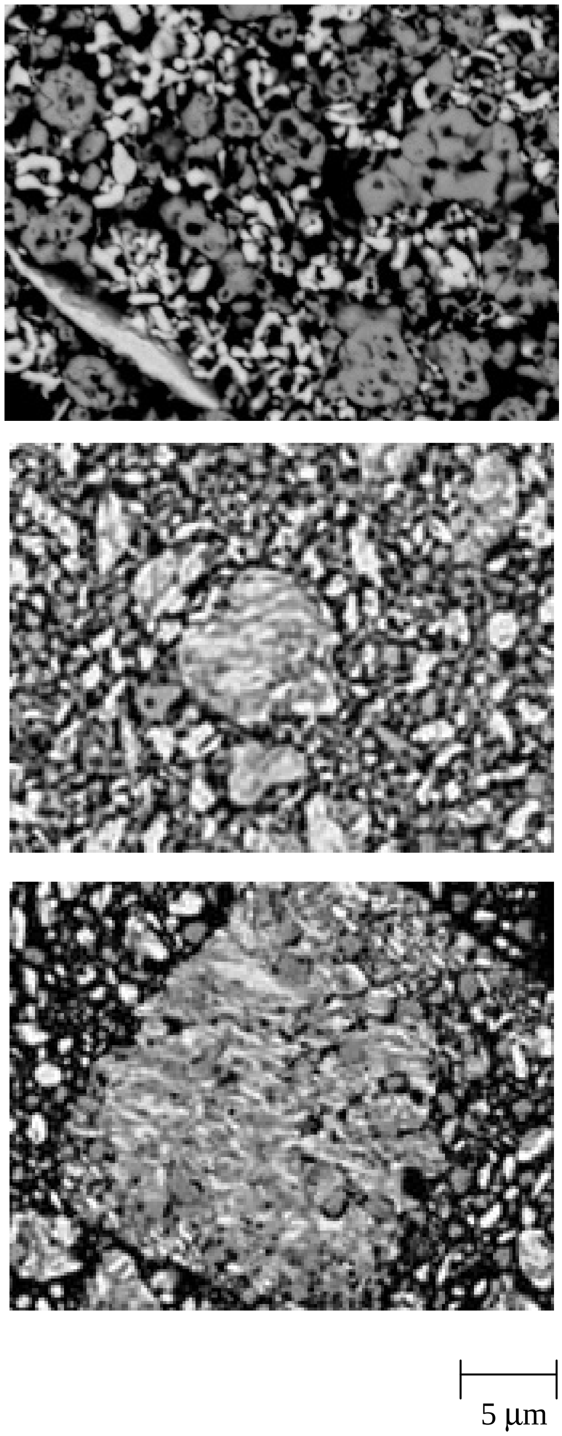

Figure 3.3: SEM images (backscattered electrons) of Co + NiO powders milled for 0.1, 1 and 20 h, in the weight ratio 1:1.

As the milling time increases, due to their ductile character, Co particles start to deform and lamellar shapes are developed, while NiO particles are progressively fractured and reduced in size. At the same time, Co and NiO grains tend to solder together and, after milling for 1 h, one obtains some FM-AFM aggregates of sizes between 1 and 5 μm. With milling time, the size of these agglomerates progressively increases and, simultaneously, new agglomerates are also created [1,2]. After milling for 20 h a large number of agglomerates consisting of Co lamellae embedded in a NiO matrix can be observed and the sizes of some of them reach 30 μm. The average thickness of the Co lamellae inside the agglomerates can be estimated to be around 0.5 μm. It is remarkable that the microstructure of these agglomerates, typical of ball-milled metal-ceramics [7], is very favorable for FM-AFM exchange interactions, since a large amount of interfaces between both components are created. A similar microstructure (i.e. FM grains embedded in an AFM matrix) is also observed in $SmCo_5$ + NiO after intermediate milling times (see figure 3.4 (a)) [3,4].

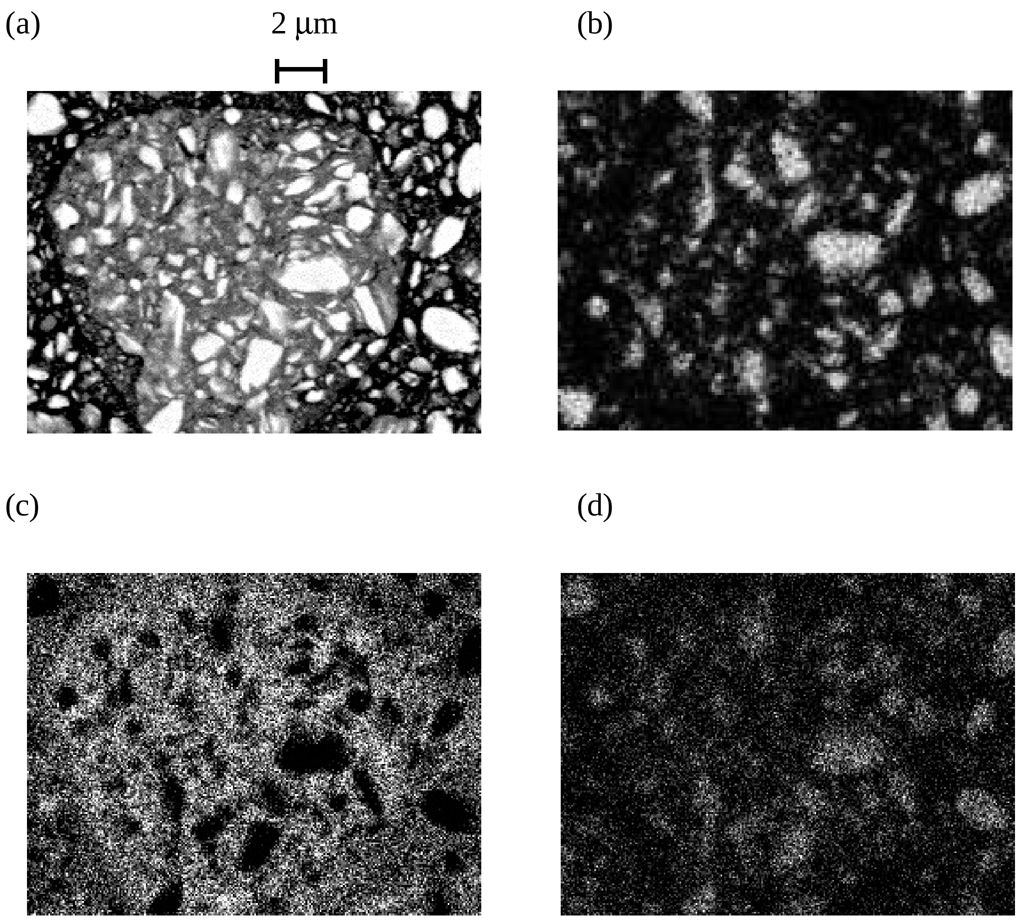

Figure 3.4: (a) SEM image (backscattered electrons) of $SmCo_5$ milled with NiO for 32 h in the weight ratio 1:1, with the corresponding Co (b), Ni (c) and Sm (d) EDX mappings

Nevertheless, if figures 3.3 and 3.4 are compared, some microstructural differences between Co + NiO and $SmCo_5$ + NiO composites can be found. For example, it can be seen that $SmCo_5$ particles in $SmCo_5$ + NiO composites, do not elongate as much as Co grains in Co + NiO composites. This may due to the different mechanical behavior of Co and $SmCo_5$ when subjected to ball milling. Actually, Co and $SmCo_5$ are found to have quite different mechanical properties. For instance, the ultimate tensile strength of Co and $SmCo_5$ are around 800 MPa and 50 MPa, respectively, which might indicate that $SmCo_5$ tend to fracture more easily than Co particles during the milling [8].

In order to identify the different components in as-milled powders, energy dispersive x-ray analyses (EDX) were carried out. For example, Co, Ni and Sm mappings, like the ones shown in figure 3.4 (b,c,d), reveal that the bright particles in figures 3.3 (a,b,c) and 3.4 (a) indeed correspond to the metallic FM (Co or $SmCo_5$), while the gray ones correspond to NiO. The black zones are mainly epoxy resin. Note that the rather sharp contrast obtained in EDX analyses indicates that the amount of atomic interdiffusion between the FM and AFM components is small. Therefore, the FM-AFM interfaces, where the FM-AFM coupling mainly occurs, are relatively well defined. As will be shown, x-ray diffraction also reveals that atomic interdifusion between the AFM and FM phases is negligible.

An analogous microstructure is encountered in ball milled $SmCo_5$ + CoO composites, as evidenced in the backscattered electrons image shown in figure 3.5 (a), which corresponds to $SmCo_5$ ball milled with CoO for 16 h. The corresponding Co and Sm EDX mappings are shown in figures 3.5 (b) and (c). It is noteworthy that the morphology observed after long-term milling in $SmCo_5$ +NiO and $SmCo_5$ + CoO composites is rather similar. Nevertheless, as will be discussed in chapter 4, the magnetic properties observed in both cases are very different, which is due to the AFM character of NiO as opposed to the PM character of CoO at room temperature.