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TEM and SEM in-situ annealing of nanocrystalline copper thin films

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Materials mechanical resistance is known to depend on the size of structural features, accordingly to the familiar Hall–Petch equation. For the nanometer range of grain sizes, this relationship breaks down and a change of the grain size exponent is needed to satisfy this dependency [1,2]. Nevertheless, the superior strength of the nanocrystalline material relays on the small dimension of its grains. Characterization of the thermal stability of these materials becomes relevant since a large fraction of atoms are in the grain boundaries and, as a result, its structure posses a large excess of energy that promotes grain growth. Grain growth in nanocrystalline metals has been observed well below the temperatures needed to promote grain growth in coarse grained materials; in some cases, even at room temperature [3]. From this perspective, the study of grain growth in nanocrystalline metals is crucial for the development of new nanocrystalline materials with outstanding mechanical properties. There are many studies that propose models to explain the mechanism of nucleation and growth of annealing twins in F.C.C. materials [4]. In-situ TEM and SEM techniques are invaluable for understanding and characterizing dynamic microstructural changes like nucleation and growth of grains and twins. This is an important observation because twinning affects the properties of materials and so is essential to comprehend the mechanism of twin formation. Other advantage of the in-situ TEM technique is the study of grain growth in ultra fine film with a thickness in the range of 50 to 100 nm. With these techniques, the mechanisms and kinetics of grain growth in nanocrystalline thin films can be observed and studied in real time.

In this work, nanocrystalline thin films of Cu, with an average grain size of 43 nm, were produced by sputtering. Upon delamination of the films, TEM samples were prepared by ion-milling in liquid nitrogen to prevent grain growth. Transmission electron microscopy (TEM) of as-deposited specimens shows that Cu thin films exhibits “equiaxial” grains with faceted boundaries and twins (fig. 1A). However the microstructure of the Cu thin films is not entirely uniform. In a few selected areas, large grains, in the range 150-200nm, were observed (fig. 1B). Subsequently, specimens were annealed by i) in-situ in the TEM at 100, 300 and 500ºC during 1, 3 and 5 hours and ii) in-situ SEM from room temperature up to 600ºC. In-situ TEM annealing at 100ºC did not induce a significant grain growth. After the 5 hour heat treatment a mean grain size of 70nm was observed (fig. 2B). TEM observations of sample annealed at 300ºC by in-situ TEM clearly show grain growth. An analysis of the grain size evolution for this specimen reveals that the average grain size after 1, 3 and 5 hours is 77 nm, 86 nm and 106 nm, respectively (fig. 2C). At 500ºC (fig. 2D) an increase in both grain size and number of twins occurred. Generally, the number and size of twins increase with temperature and annealing time. As expected, the kinetics of grain growth is significantly faster at 500ºC. After 1, 3 and 5h the grain size at this temperature is 175 nm, 237 nm and 278 nm, respectively.

SEM observations of the thin film surface reveal small features, with sizes ranging from 125 to 750 nm and a mean size of 409nm (fig. 3A). The size of these features, ten times larger then the grain size measured by TEM, discards the possibility of corresponding to individual grains; these features must represent clusters of grains in columns, as represented in Fig. 3B. In-situ SEM annealing up to 399ºC did not cause significant variations in structural features of the film surface, the mean size increased to 539nm (fig 4A). Raising the temperature to 500 and 600ºC changes the morphology of the surface (fig. 4B and 4C). At 600ºC, grain boundaries and twins inside the grains are clearly observed (fig. 4D), instead of the clusters observed at lower temperatures. A few large grains coexist with small grains as a result of an abnormal grain growth process. These observations are confirmed by the bimodal grain size distributions detected at these temperatures. The mean grain size at 500 and 600ºC is 584nm and 611nm, respectively.

In-situ TEM and SEM annealing observations cannot be compared; TEM observations reveal grain boundaries and twins whilst SEM reveal clusters of grains, except for high temperature. However, some results are consistent: low temperature annealing did not produce considerable structural alterations; significant grain growth and twinning occurs at high temperature annealing. At 500 and 600ºC in-situ SEM promotes abnormal grain growth and a coarse structure is observed. The same film observed by in-situ TEM at 500ºC exhibits a finer grain size as a result of a normal grain growth process.

The difference in grain growth behaviour between the in-situ TEM and SEM is not fully understood. We believe the cause is related with the fact that during in-situ TEM annealing grain growth occurs in 2D (thin film conditions), whereas during in-situ SEM occurs in 3D (thick film conditions). In thin films (2D) the energies of top and bottom surfaces of the film can have a strong influence on grain growth while in thick films (3D) grain boundary energy is more important. Another important aspect in thin films grain growth is groove formation where grain boundaries intersect the surface of the film. These grooves can reduce the mobility of grain boundaries and cause grain growth stagnation that became more important in 2D. Abnormal grain growth was only observed in in-situ SEM samples (3D).The number of defects in 3D films is higher than in 2D. The number of faceted grain boundaries increase with thickness because the number of grains increases. These faceted grain boundaries have a smaller interfacial energy and are less mobile than the curved ones, promoting abnormal grain growth.

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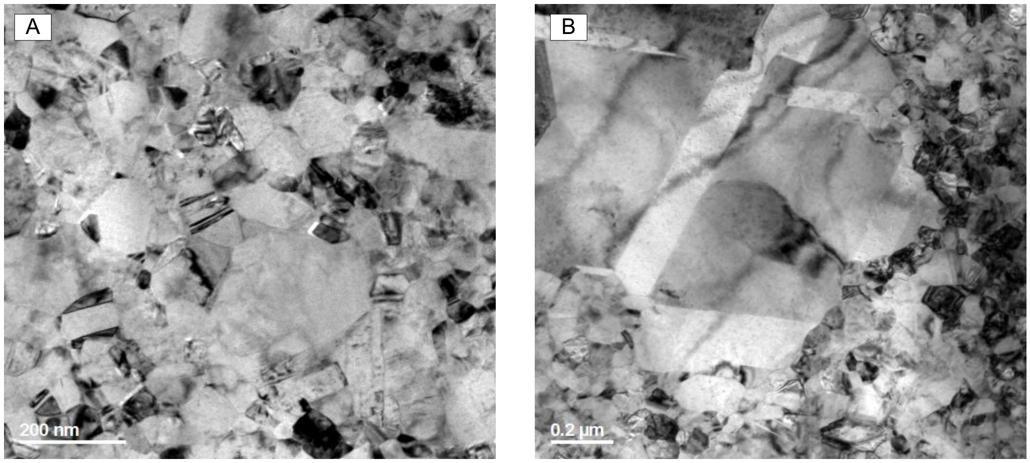

Fig. 1 – TEM observations of as-deposited nanocrystalline copper thin film A. Bright field; B. TEM observations where a region with non-uniform grain size distribution can be observed.

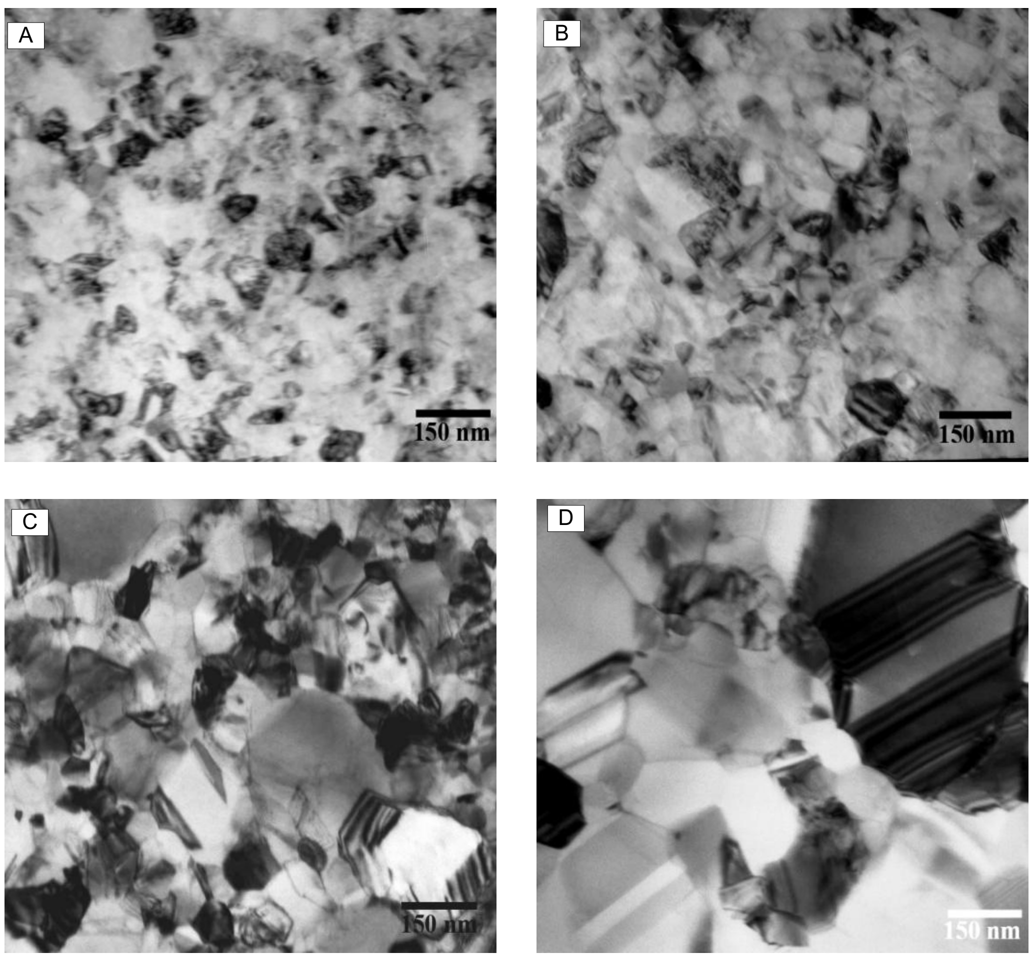

Fig. 2 - Bright field TEM observations of nanocrystalline copper thin film. A. as-deposited; B. in-situ annealed at 100ºC for 5h; C. in-situ annealed at 300ºC for 5h; D. in-situ annealed at 500ºC for 5h;

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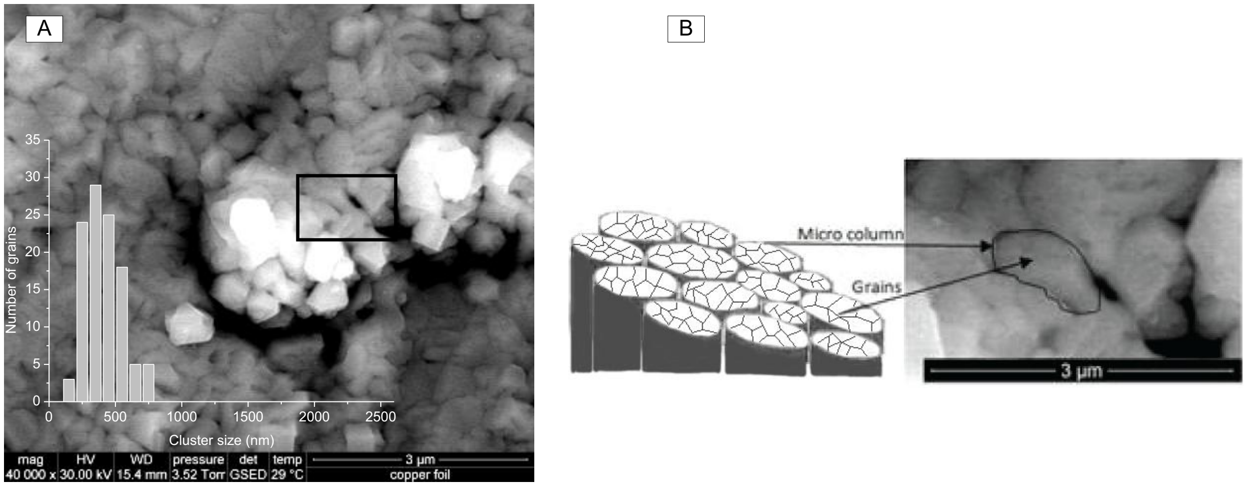

Fig. 3 – A. SEM images and cluster size distribution of the nanocrystalline copper thin film. B. Detail of the structure and schematic representation of micro column with a cluster of grains.

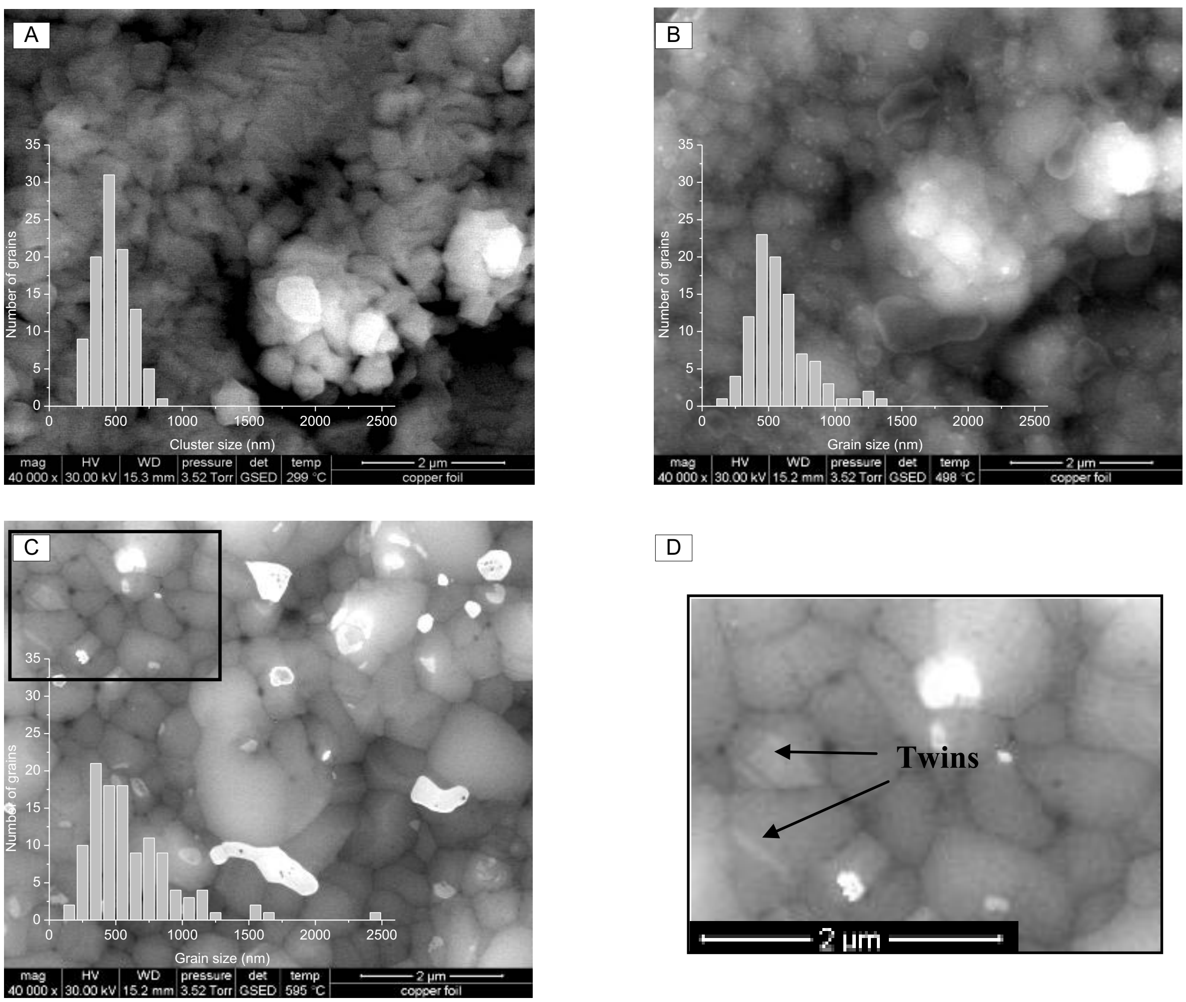

Fig. 4 - Sequence of in-situ heating SEM images and cluster/grain size distributions of nanocrystalline copper thin film. A. 299ºC; B. at 498ºC; C. at 595ºC; D. Detail of C showing twins.

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