Nanograin formation in milled MoO$_3$ powders

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Abstract. Powder of Molybdenum trioxide was milled for different times in horizontal ball mills. Such powder was characterized by TEM and XRD. Powder was rapidly de-agglomerated and fragmented up to attain nanoplates of two types, amorphous and crystalline. Finally, cold-welding of nanoplates occurred permitting some relaxation process to obtain a more stable energized structure consisting of equiaxial crystalline nanograins after 16 hours of milling.

1. Introduction

It is known that a nanostructure in powders is currently obtained by ball milling. Phenomena as deformation, fracture and cold-welding occur, predominating one of them if powders are ductile or fragile [1]. The microstructural evolution during milling of fragile powders indicates that fragmentation and aggregation of particles predominate until reach a limit in particle size, after this, conditions are favorable for the cold welding or other material transfer mechanisms.

During milling of ductile powders, defects are created and rearranged, permitting the formation of a stable “energized” structure consisting of nanograins [2]. Understanding of how nanograins are attained in fragile materials by milling is not clear. By other hand, orthorhombic MoO$_3$ powder is a material that consists of agglomerates of monocristalline plates bonded by Van der Waals forces [3], which if they were milled, probably showed a clear transition step to obtain an equiaxial nanograin structure. Mestl et al [4] followed mainly by XRD the microstructural evolution of milled MoO$_3$ powders, where they found that the grinding process seems to proceed via two steps: disintegration of larger particles or agglomerates and finally a continuous fragmentation of primary cristallites. A TEM study is needed to get a better understanding how nanograin is formed during milling of MoO$_3$ powders.

2. Experimental

MoO$_3$ powder obtained by roasting of molybdenum concentrates (Molymex S.A. de C.V.) with a nominal purity of 99.44% and a mean particle size of 100 μm was used. Millings of powder were done at 0.5 h, 4 h, 8 h and 16 h in stainless steel mills of diameter of 12.5 cm. 2.461 Kg of hardened steel balls with sizes of 1.27 cm were utilized. Millings were carried out at 110 rpm for different times under air atmosphere. A ball-to-powder volume ratio of 90 was chosen as optimum for this powder after some previous experiments. An ultra high resolution transmission electron microscope (TEM) Jeol, JM2100 with a LaB$_6$ filament was used at 200 KV. Sigma ScanPro V 5.0 software was used for image analysis. An X-Ray diffractometer Philips, X’Pert,
with a secondary graphite monochromator was employed to obtain XRD patterns with a step of 0.03° and a time per step of 1 second. Monochromatic Cu Kα1 radiation was used.

3. Results and discussion

3.1 X-ray diffraction of MoO3 powders milled for different times

It is seen in figure 1 that intensity of peaks of MoO3 milled for 16 hours is smaller than that of the un-milled ones and a broadening of its width is also visible, which means that a nanograin structure was attained at that milling time. Impurities of MoO2 and SiO2 phases are present in un-milled powder.

![Figure 1. X-ray diffraction patterns of MoO3 powder milled and unmilled (0 h). Impurities of MoO2 and SiO2 are detected. Powder Diffraction files from the ICDD used to identify MoO3, MoO2 and SiO2 phases were 00-035-0609, 01-076-1807 and 00-083-0539 respectively. MoO3 phase crystallizes in the orthorhombic lattice (space group Pbnm (62)).](image)

3.1. De-agglomeration, fragmentation and cold-welding of monocrystalline plates

Mestl et al studied the milling of MoO3 powder mainly by XRD [4]. They described the grinding process as a de-agglomeration and fragmentation of monocrystalline plates involving amorphization of their surface. TEM photomicrographs of figure 2 show these different steps in MoO3 powders milled at 0.5 h, 4 h and 8 h in the present work.
Figure 2. Bright field TEM images of MoO$_3$ powder milled: (a) 0.5 h, (b) 4 h and (c) 8 h. (d) SAD pattern of (b) showing a broader ring next to the central beam.

A continuous de-agglomeration and fragmentation of plates happen during the early milling times (see figure 2a) until reach some limit size at intermediate times (for example, 4 or 8 hours). After this, a possible exfoliation of nanoplates happens that liberates monolayers. Two types of monolayer nanoplates are observed, amorphous and crystalline ones. Also, at intermediate times of milling, cold-welding of nanoplates occurs, resulting in microparticles where individual nanoplates are still visible at its border (see figures 2b and 2c). The amorphous phase is detected by a broader ring in the selected area diffraction (SAD) pattern showed in figure 2d.

3.2. Limit size in Nanoplates and nanograins

High resolution TEM views show the amorphous or crystalline nature of the nanoplates. The amorphous ones are showed in figure 3a where some characteristic rounded zones at the interior of the nanoplates are clearly seen. A crystalline nanoplate is shown in figure 3b.

Figure 3. High resolution TEM images of MoO$_3$ powder milled 8 hours: (a) Amorphous and (b) crystalline nanoplates.

At long milling times (16 hours) microparticles are composed of only equiaxial crystalline nanograins as seen in figure 4. A complete disappearance of nanoplates suggests that some kind of recovery of crystalline nanoplates and recrystallization of the amorphous ones occur such that a lower-energy structure is formed as equiaxial crystalline grains. Internal energy that promotes such relaxation process must be stored at the surface of nanoplates but also in the disorder structure of the amorphous phase.

Figure 4. TEM images of MoO$_3$ powder milled for 16 h: (a) Bright field and (b) dark field images.

During the milling of MoO$_3$ powders a limit in size is attained for both, nanoplates and nanograins. Table 1 shows that amorphous nanoplates are wider than crystalline ones. The
equiaxial grain is smaller than the width of crystalline nanoplates. Some dimensional factor, related to surface area could be influencing the transition of amorphous-to-crystalline phase in nanoplates to attain a minimum value of surface stress [5]. A study to explain the presence of amorphous and crystalline nanoplates is under current.

| Table 1. Width of nanoplates and Feret Diameter of equiaxial nanograins. |
|-------------------------------------------------------------|
| Nanoplates | Amorphous (nm) | Crystalline (nm) | Grain size (nm) |
| mean       | 16.13          | 6.09            | 3.81            |
| Standard deviation | 6.29          | 2.36            | 2.48            |
| Sample size  | 23             | 68              | 351             |

4. Conclusions
A more complete description of the microstructural evolution of milled MoO$_3$ powders suggested by Mestl et al [4] has been done in the present work. Observations by TEM suggest that during milling of MoO$_3$ powders a rapid de-agglomeration and fragmentation of monocristalline plates is happening at short milling times. A limit in size of nanoplates is attained mainly in its width during intermediate milling times. Some kind of exfoliation occurs of these nanoplates until monolayers are observed. Two types of monolayer nanoplates are seen, amorphous and crystalline ones. Also during intermediate milling times cold-welding of monolayer nanoplates predominates forming microparticles where individual monolayer amorphous and crystalline nanoplates are still observed at its border. At long milling times no more nanoplates are observed. Microparticles are composed of only equiaxial crystalline nanograins. Such fact suggests that a relaxation process occurred.

5. References
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