APPLICATION OF THE XPS TECHNIQUE ON THE CHARACTERISTICS OF THE MOLYBDENUM PARTS RECYCLED IN A PLANETARY MILL

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Abstract. *The use of Mechanical Alloying technique as a tool to recycling Molybdenum electric resistances used in furnaces/ovens was investigated. In order to study the efficiency of the milling, the phases obtained after milling of Mo powder were investigated as a function of the milling time (4h, 8h 16h and 24h) and also of the ball to powder weight ratio (98:1, 49:1, 32:1, 25:1, 20:1, and 16:1), using x-ray diffraction and Rietveld refinements of the diffraction patterns and the XPS technique. The results indicate the presence of Mo, Mo_2C and a-Fe, being Mo the majority one, and the others are contaminant phases. It was also observed the presence of COO^- bonding on the powder particle surfaces, resulted from the solid lubricant used on the milling process. The use of 30:1 ball to powder weight ratio optimizes the milling efficiency. The results indicate that Mo can be recycled using Mechanical Alloying.*

 Key words: Molybdenum, Recycling, High Energy Milling.

1 – INTRODICION

Mechanical Alloying (MA) was invented originally as a method for production of nickel alloys hardened by dispersion of oxide phases [1], but now this technique is used in order to produce stable and metastable materials, amorphous alloys and nanostructured materials [2]. Due to the introduction of energy during the milling process, chemical reactions can happen in the vial, and formation of new alloys can take place.

MA has some interesting advantages when compared to other techniques. It is relatively simple and the equipments used are of easy operation. There is the possibility of scaling up and it can be used to produce alloys that cannot be or at least are very difficult to obtain by other techniques, for technical or economical reasons (or both). This is the question about the recycling of molybdenum, proposed here. Molybdenum, which is a refractory metal, has many interesting physical-chemical properties and, from the technological point of view, it is used in production of steels due to the improvement in corrosion resistance and in the creep resistance [5, 6]. It is also used in fabrication of gas fans and electrical resistance of furnaces [7, 8] and its recycling is very difficult, as it occurs with other refractory metals.

To date, only scattered X-ray photoelectron spectroscopy (XPS) data have been vailable on the molybdenum system. Three reports in the literature have treated this problem very briefly. Spevack and Manthiram have examined some fairly common molybdenum compounds (mainly molybdates) and have

pointed out the application of XPS as an analytical technique for the determination of MoO_2-MoO_3 mixtures [9,10,11].

Here we investigated the milling of small pieces of molybdenum as a function of the parameter ball to powder ralation. The results are discussed in terms of the average particle size obtained for different size ranges, which present technological interest, since powder flowability is directly related to the average particle size [12].

2 - EXPERIMENTAL PROCEDURES

2.1 – Materials and methods

The raw material used consisted of small carbon-contaminated molybdenum pieces with average sizes of 3 x 5 x 0.8 mm, obtained from broken electrical resistances used in furnaces for heat treatment. They were sanded and washed with ethanol. Then, some pieces were put in two tempered steel vials with 250 mm^3 each, together with 15 steel balls with diameter 20 mm. The milling speed 150 rpm they had been kept constant. In addition, a small quantity of zinc stearat 0.03 g (0.2 wt.%) was used in order to avoid powders sticking to the balls and vial inner walls.

The vials were sealed under air atmosphere, and several milling times (4 h, 8 h, 16 h and 24 h). The relation in ball to powder weight ratio it was studied using (5, 10, 15, 20, 25 and 30 g) and balls was about 490 g for each vial (the BPR used was 98:1, 49:1, 32:1, 25:1, 20:1, and 16:1) were considered in this study.

2.2 – Planetary Mill

The milling used was a planetary Fritsch Pulverisette 5 mill, available at LTPP (Laboratório de Tecnologia de Pós e Plasma). In order to avoid overheating, the process was run in batches of 20 min of milling and 20 min of dead time. After each milling, the powder obtained was sieved using the sieves 65 MESH (212 µm), 80 MESH (180 µm), 100 MESH (150 µm), 115 MESH (125 µm), 170 MESH (90 µm) and 200 MESH (75 µm).

2.3 – X ray diffraction (XRD)

Then, x-ray diffraction patterns were obtained using a Shimadzu D7000 difractometer, available at LORXI (Laboratório de Óptica de Raios-X e Instrumentação), working with the CuK_α line (λ = 1.5418 Å) at θ-2θ geometry. The morphology of the powders was investigated using a FEI Quanta 200 scanning microscope.

2.3 – X-ray photoelectron spectroscopy (XPS)

The XPS spectra were taken using a commercial VG ESCA 3000 system. The base pressure in the experimental chamber was in the low 10^{-9} mbar range. The spectra were collected using Mg Ka (1253.6 eV) radiation and the overall energy resolution was about 0.8 eV. Samples of 0.6 cm^2 were used. Survey spectra were recorded for the samples in the 0 –1100 eV kinetic energy range by 1 eV steps while high resolution scans with 0.1 eV steps were conducted over the following regions of interest: C1s, O1s and Mo 3d.

Surface charging effects were compensated by referencing the BE (binding energy) to the C1s line of residual carbon set at 284.6 eV. Spectral decomposition assumed mixed Gaussian–Lorenzian curves and was performed by using background subtraction and a least square fitting program.

Sputtering of the sample surface was performed with an argon ion gun under an accelerating voltage of 3 kV. All the samples were measured after 13 min of Ar sputtering.

3 – RESULTS AND DISCUSSION

3.1 – High Energy Milling

Table 1 shows the amount of powder obtained considering different average particle sizes after the powder sieving.

Table 1 – Amounts of powders obtained as a function of the ball to powder relation.

Average particle size - P (μm)	Sieve (MESH number)	Amount of powders for each weight ratio (g)					
		5g (98:1)	10g (49:1)	15g (32:1)	20g (25:1)	25g (20:1)	30g (16:1)
$P > 212$	+ 65	4.44	9.22	10.56	17.27	22.74	28.75
$180 < P \leq 212$	- 65 + 80	0.15	0.14	0.55	0.34	0.27	0.1
$150 < P \leq 180$	- 80 + 100	0.19	0.16	0.99	0.53	0.3	0.1
$125 < P \leq 150$	- 100 + 115	0.19	0.16	0.49	0.4	0.24	0.15
$90 < P \leq 125$	- 115 + 170	0.17	0.11	0.7	0.27	0.26	0.14
$75 < P \leq 90$	- 170 + 200	0.27	0.26	0.15	0.2	0.7	0.26
$P \leq 75$	- 200	0.29	0.21	1.2	1.22	0.85	0.42
Total (g)		5.7	10.53	14.51	20.23	25.36	29.92

The powders obtained were classified according to the following three categories:
- Type A: powders with average particle size larger than 150 μm.
- Type B: powders with average particle size ranging from 90 to 150 μm.
- Type C: powders with average particle sizes smaller than 90 μm.

Figure 1 shows the behavior of the evolution of the fractions weight ratio for each of the three types of powder studied (types A, B and C), defined in table 1, in a function of the relation in weight ratio of ball to powder.. It is interesting to notice that the fraction of the powder in the type B if practically kepped linear for relations or BPR of 98:1 and 49:1. However for relation of 32:1 it has a weight increase in the powder type B, what it can be associated with the optimization of the useful space in the milling vase (ball + powder) what it makes with that the milling if becomes efficient. Already it stops lower relations 25:1, 20:1 and 16:1 the some of the weight of the fractions of after come back to be linear becoming the inefficacious milling.
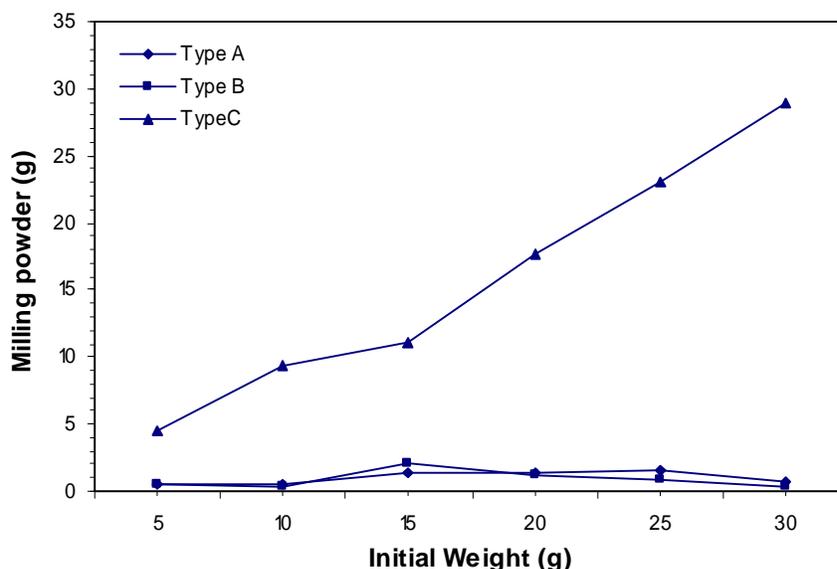

Figura 1 - Evolution of the amount of powder for types A, B and C as a function of the ball to powder ralation, for 150 rpm and 4h.

3.2 – CHARACTERIZATION BY X-RAY DIFFRACTION

The powders obtained were studied using the x-ray diffraction technique followed by a Rietveld refinement procedure [13]. The investigation of the x-ray diffraction patterns for 4 h, 8 h, 16 h and 24 h,150 rpm and ball to powder ralation 32:1 indicated that the main phase present in the milled samples is

the crystalline Mo phase (JCPDS 42-1120). There are also two other contaminant phases, the phase Mo_2C (JCPDS 790744), probably associated with a contamination of the raw material by carbon, and the phase α-Fe (JCPDS 870721), associated with a contamination by the milling media. Figure 2 shows the results obtained for the four milling times listed above and also their simulations using the Rietveld method.

Table 2: Structural data for the Mo samples obtained from the Rietveld refinement procedure of the X-ray diffraction patterns shown in Figure 2.

Milling time	Phases	Lattice parameter (Å)	Relative amount of phase (%)	Average crystallite size (Å)
4 h	Mo JCPDS 421120	$a = 3.1495$	93	260
	Mo_2C JCPDS 790744	$a = 4.7518$ $b = 6.0526$ $c = 5.1708$	5.5	
	Fe JCPDS 870721	$a = 2.8723$	1.5	
8h	Mo	$a = 3.1514$	83	336
	Mo_2C	$a = 4.7556$ $b = 6.0346$ $c = 5.1945$	15	
	Fe	$a = 2.8700$	2.0	
16 h	Mo	$a = 3.1504$	90	257
	Mo_2C	$a = 4.7675$ $b = 6.0134$ $c = 5.1960$	9,3	
	Fe	$a = 2.8731$	0.7	
24 h	Mo	$a = 3.1469$	87	154
	Mo_2C	$a = 4.7742$ $b = 6.0171$ $c = 5.1811$	11.5	
	Fe	$a = 2.8702$	1.5	

The relevant structural parameters obtained for these samples are shown in Table 2. Table 2 shows lattice parameters and relative amount of phases for all phases present in the samples. It only shows the average crystallite sizes of the Mo phase because the small amount of the other phases makes the determination of this quantity very imprecise. The lattice parameters and the average crystallite size of Mo phase increase from 4 h to 8 h, and after that they decrease. This fact could be associated with an initial increase in the system stress, which is released after a determined milling time is achieved. In the beginning, the crystallites are forced together, and their average sizes are increased. As more and more energy is given to the system, they change to a more stable situation, were the average crystallite size and also the lattice parameter is smaller. This can also be seen if the average particle size is considered. Table 2 shows the amount of powder obtained considering different average particle sizes after the powder sieving.

3.3 – CHARACTERIZATION BY X-RAY PHOTOELETRON SPECTROMETRY

Figure 3 shows XPS specter and analysis of the peak "O1s", in pieces and molybdenum powder as a function of the milling time.
Analyzing the specter of oxygen it was possible to verify a significant increase in the peak of oxygen in molybdenum (pieces) after made the cleanness. This increase can be associated with the fact of that, before the cleanness, he was submerged for underneath of pieces. However, in the powder samples is possible to verify that to the measure that increases the milling time, it also increases the amount of oxygen, fact this can be explained by the greater numbers of existing free surfaces, in long times of milling and consequence oxidation.
Figure 4 shows XPS specter and analysis of the peak "C1s", in pieces and molybdenum powder as a function of the milling time.
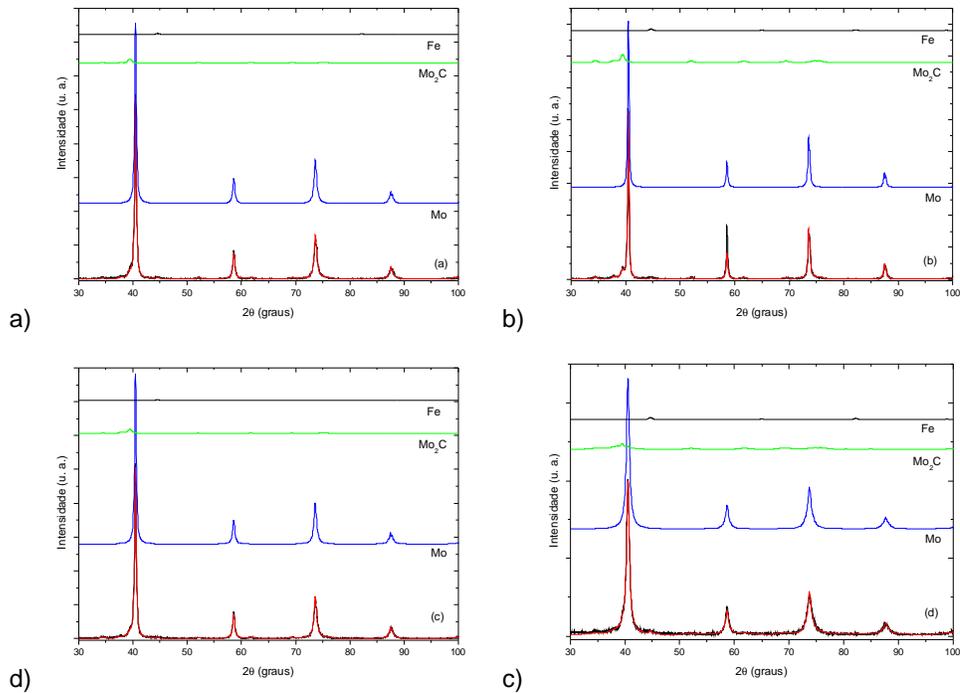
a)

b)

d)

c)

Figure 2: X-ray diffraction patterns (bottom black lines) for Mo samples milled using 150 rpm for (a) 4 h, (b) 8 h, (c) 16 h and (d) 24 h, and their simulations (red lines) using the Rietveld method considering the phases Mo (blue lines), Mo_2C (green lines) and α-Fe (top black lines).
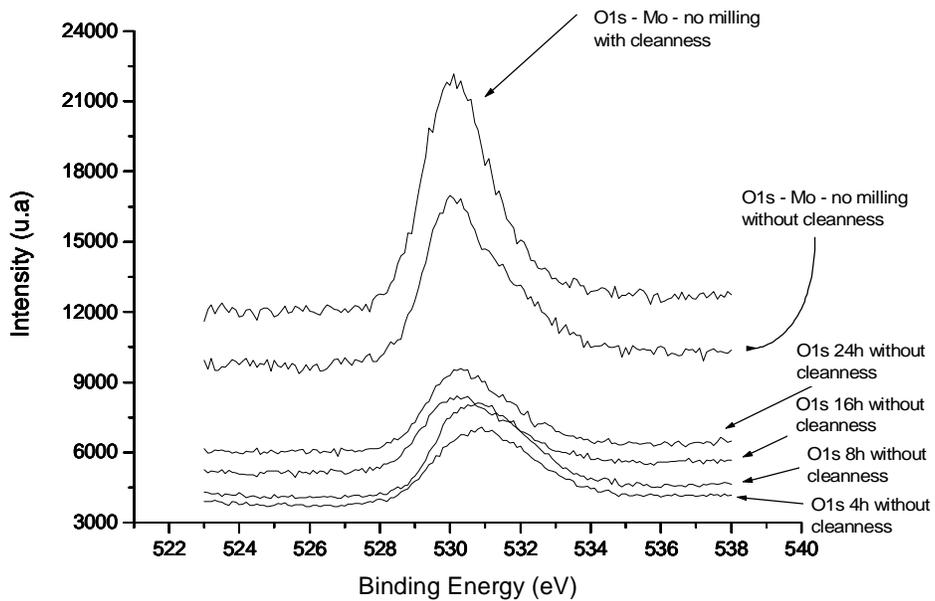

Figure 3 – Specter of XPS and analysis of the peak "O1s": samples of molybdenum in pieces; e samples of molybdenum milling as a function in the milling time.

Analyzing the specter of carbon, in molybdenum (pieces) it was possible to verify that before the cleanness a great amount of superficial carbon exists, and that after the cleanness the same

diminishes significantly. Is fall this associate with the great amount of carbon in the surface. After the cleanness this carbon diminishes significantly demonstrating that the carbon is only in the surface.

However in the powder samples it was possible to verify that it has a carbon increase in function of the milling time, fact this can be on with a bigger amount of existing free surfaces, what it would imply around in a bigger amount of solid lubricant (zinc stearate) of particles. This lubricant also appears under the form of radical COO⁻ in the specter shows in figure 4 (285,00 ± 4.41) [9].

Figure 5 shows XPS specter and analysis of the peak "Mo3d", in pieces and molybdenum powder as a function of the milling time.
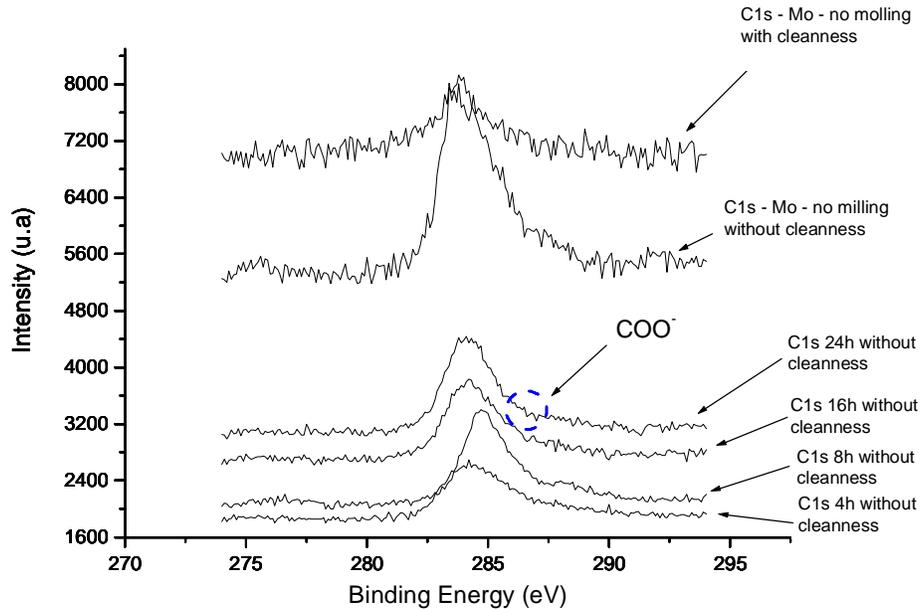

Figure 4 – Specter of XPS and analysis of the peak "C1s": samples of molybdenum in pieces; e samples of molybdenum milling as a function in the milling time.
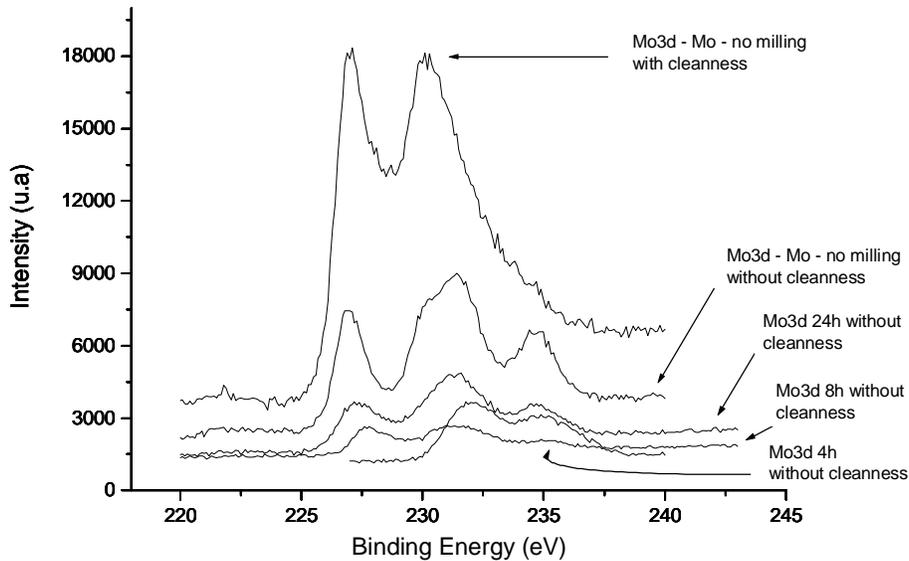

Figure 5 – Specter of XPS and analysis of the peak "Mo3d": samples of molybdenum in pieces; e samples of molybdenum milling as a function in the milling time.

Analyzing the specter of the Molybdenum (pieces) it is verified that without the superficial cleanness it appears the pure Molybdenum, and the MoO_3 composition. When the trioxide is made the cleanness disappears. This can be associated with the fact of molybdenum oxide to be superficial [11]. When if it makes the bombardeamento is pulled out and only pure molybdenum appears. However in the samples of milling powder in a function of the time, the pure Molybdenum and the Molybdenum Trioxide appear both.

4 – CONCLUSION

a) The Mo electric resistances used in furnaces/ovens can be recycled using the Mechanical Alloying technique, and a micrometric powder with nanometric phases can be obtained.

b) The study of the BPR it made possible to evidence that the 32:1 relation is most efficient, in view of that this can be associated with the useful space inside of the milling vase (balls + powder).

c) The powder obtained is formed, basically, by the Mo phase, and a small contamination of the raw material by carbon is responsible for the appearance of the Mo_2C phase. A very small quantity of α-Fe phase due to the milling media also appears in the powder. Rietveld refinements furnished structural data as lattice parameters, amount of phases and average crystallite sizes.

d) For the XPS technique it was evidenced existence of elements (Mo, C and O) and MoO_3 composition, in the same resistence before being worn out (in pieces). Also it was possible to verify the existence of radical COO^-, proceeding from the solid lubricant in all the samples that had been milling out in function of the milling time.

5 – REFERENCES

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