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# HIGH ENERGY MILLING EFFECT IN PARTICLE SIZE DISTRIBUTION AND CELLS PARAMETERS OF THE WC-10wt.%CO COMPOSITE

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**Resumo:** *Nacrystalline WC-10wt.%Co powders were prepared by high energy milling and liquid phase sintered. The powders with different milling time were characterized by particle size distribution, mean diameter and cells parameters. The milling time caused a particle size reduction and mean diameter reduction. The cells parameters of the phases WC, Co-hc, Co-cfc in WC-10wt.%Co composite powders decreasing at milling time increase. . For the composites sintered the cells parameters of the phases WC, Co-hcp and Co-fcc it is practically constant for the axial relations "a". For the axial relations "c" at milling time increase the cells parameters in WC-10wt.%Co composite powders for the WC and Co-hcp phases increase until milled at 2 hours compared with starts materials, after 2 hours at milled until 300 hours decrease. At milling time increase the cells parameters in WC-10wt.%Co sintered composite for the WC phase decrease until milled at 300 hours compared with starts materials The cells parameters of the Co-hcp phase until milled at 2 hours increase compared with starts materials, after 2 hours at milled until 100 hours decrease. After 100 hours at milled until 200 hours decrease*

***Key Words:*** *High energy milling, particle size distribution, mean diameter and cells parameters*

## 1.0 INTRODUTION

THE MAIN CLASS OF HARD METAL IS A COMPOSITE, CONSISTING OF A CERAMIC PART, TUNGSTEN CARBIDES (WC) AND METALLIC PART, COBALT (CO). IT IS USED FOR CUT TOOL, IT HAVE GOOD MECHANICAL PROPERTIES AS: HIGH HARDNESS, BREAKING GOOD RESISTANCE AND HEAT RESISTANCE. ALL OF THESE PROPERTIES DEPEND OF THE MATERIAL MICROSTRUCTURE THAT IT COME FROM THE MATERIAL PROCESSING AND SINTERING, FOR EXAMPLE: THE TENACITY AND HARDNESS GROW WITH REFINEMENT POWDER OF WC AND CO. THE HIGH ENERGY MILLING IS AN IMPORTANT CONTRIBUTION FOR THIS PROCESS, ZHANG, ET AL (2003). THE MILLING IS A SUFFICIENTLY PROCESS TO USED TO PREPARE NANOCRYSTALLINE, HARD METAL, AMORPHOUS ALLOY, METALLIC ALLOY AND NITRITES METAL. BECAUSE IT IS THE SIMPLIFIED PROCESS IN RELATION THE INITIAL WC-CO POWDERS PREPARED BY SPRAY CONVERSION PROCESS FROM AQUEOUS SOLUTION CONTAINING AMT (AMMONIUM METATUNGSTATE) AND $CO(NO3)_2$, AND FOLLOWED BY OXIDATION, REDUCTION AND CARBONIZATION PROCESS. WITH THE HIGH ENERGY MILLING IS POSSIBLE TO GET IN 32 MINUTES NANOCRYSTALLINES PARTICLES WITH GRAIN SIZE AROUND 35 TO 25 nm FOR THE COMPOSITE WC-10%CO, F. L. ZHANG, ET AL (2003).

NANOCRYSTALLINE WC-CO POWDERS ARE PRESENTLY USED FOR PRODUCING CEMENTED CARBIDES WITH FINER MICROSTRUCTURE. THE FINE GRAIN SIZE CAME FROM OF THE HIGH ENERGY MILLING CAUSED VARIATION IN STRUCTURES PARAMETERS AS: CELLS PARAMETERS, SURYANARAYANA (2001).

THIS WORK, A STUDY THE EFFECT OF HIGH ENERGY MILLING IN PARTICLE SIZE DISTRIBUTION, MEAN DIAMETER AND CELLS PARAMETERS.

## 2.0 EXPERIMENTAL PROCEDURE

The start materials were WC powders with particle size of 0,57$\mu$m, manufactured by WBH in Austrian and Co powders with particle size of 0,95 $\mu$m, manufactured by HC Stark in Germany. In the powders was added graphite powder to supply carbon loss during the processing. It also was added paraffin to serve as lubricant during compacting process. The composition was the same for all samples.

The nanostructured powders of WC-Co were prepared in a planetary mill Fritsch Pulverisette 7, at deferent times. After this process the powders were dried through at Rota vapor. Dry mechanical mixed was carried out in planetary ball mill at 1/6h. The X-ray diffraction was carried out in Shimadzu-XD600 difractometre, with CuK$\alpha$ (1,5418Å) radiation with tension 30kv and 20mA. The samples of the WC-10wt.%Co were compacted in stainless steel die with cylindrical county of 10 mm of diameter, at a pressure of 200 Mpa. The compacted samples were sintered in a resistive furnace at argon atmosphere at 1400 ºC by 5 min. The particle size distribution and mean diameter analysis was carried out in a Granulometro Cilas model 920 L and 1180. The cells parameters were calculated though Rietveld method analyzes.

## 3.0 RESULTED AND DISCUSSION

The Figure 1 show the particle size distribution of WC powder and Co powder when can be see that for the particle size of Co is minor than 10 µm, with a mean diameter of 3,90 µm and in WC the particle size is minor than 10 µm, with a mean diameter of 1,46 µm.

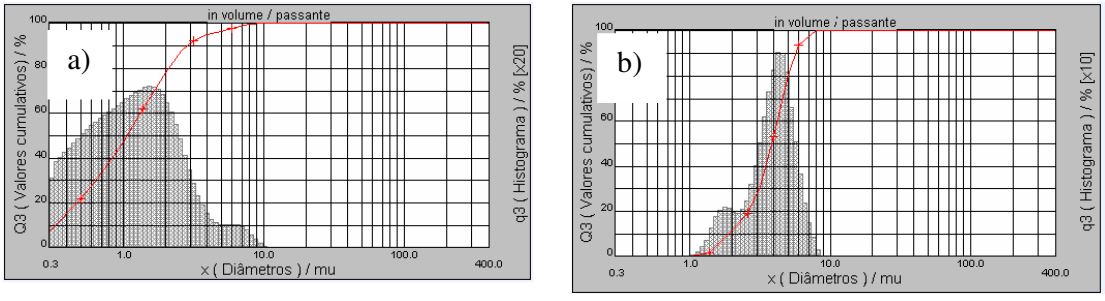


**Figure 1. Particle size distribution of a) WC powders and b) Co powders.**

The figure 2 show the particle size distribution of the WC-10wt.%Co mechanical mixed and milled at 2h. The particle size distribution in powder mechanical mixed is minor than 17 µm, with a mean diameter of 2,05 µm. Comparison the figures 1 and 2 can be affirmation that have a amount of WC and Co agglomeration, this effect can be justified though the pick in 10 µm of the Co in figure 2. The particle size

distribution in powder mechanical mixed is minor than 30 µm, with a mean diameter of 3,79 µm. This values are major than the powders mechanical mixed because the milling time caused a minor cold welding and the appearance the little agglomerations of WC.

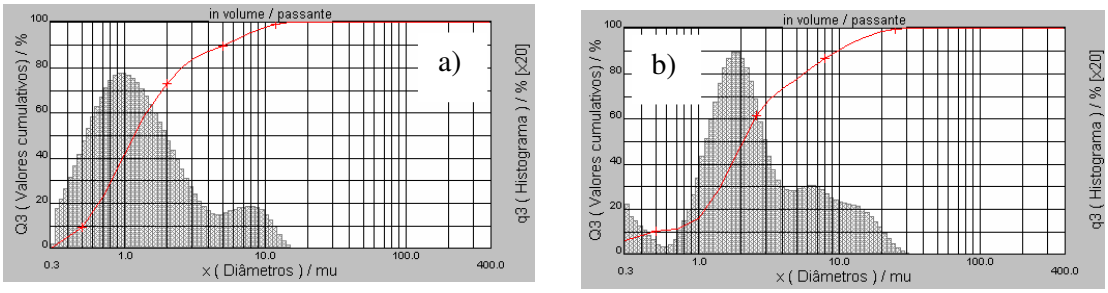


**Figure 2. Particle size distribution of WC-10wt.% Co powders a) mechanical mixed and b) milled at 2h.**

The figure 3 show the particle size distribution of the WC-10wt.%Co milled at 100h and milled at 200h. The particle size distribution in powder milled at 100h is minor than 16 µm, with a mean diameter of 2,91 µm. This values are major than the powders milled at 2h this effect came from of the particle reduction at milling time increase. The milling time caused the cold welding and amount of the agglomeration of WC e Co that also influenced these values. The particle size distribution in powder milled at 200h is minor than 12 µm, with a mean diameter of 1,51 µm. This values are minor than the powders milled at 100h this effect came from the particle size reduction at milling time increase. The amount of the cold welding, fracture and agglomeration of WC at milling time increase influenced in value of mean diameter.

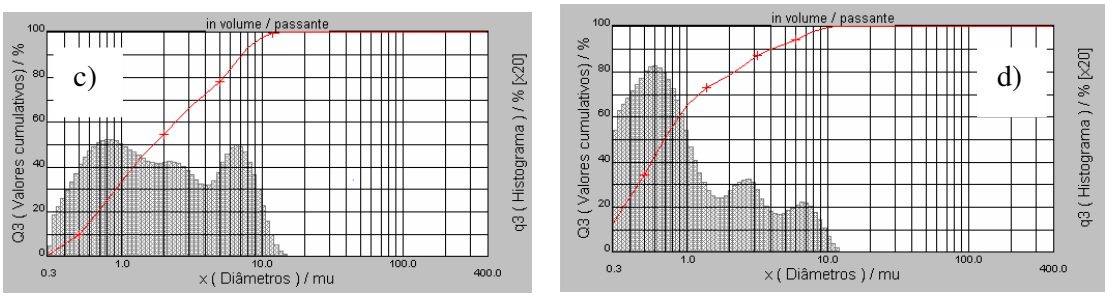


**Figure 3. Particle size distribution of WC10wt.% Copowders c) milled at 100h and d) milled at 200h.**

The figure 4 show the particle size distribution of the WC-10wt.%Co milled at 300h when can be see that for the particle size is minor than 12 µm, with a mean diameter of 1,76 µm. The mean diameter of the composite powder milled at 300h is major than 200h, this effect is related the a possible cold welding between particles.

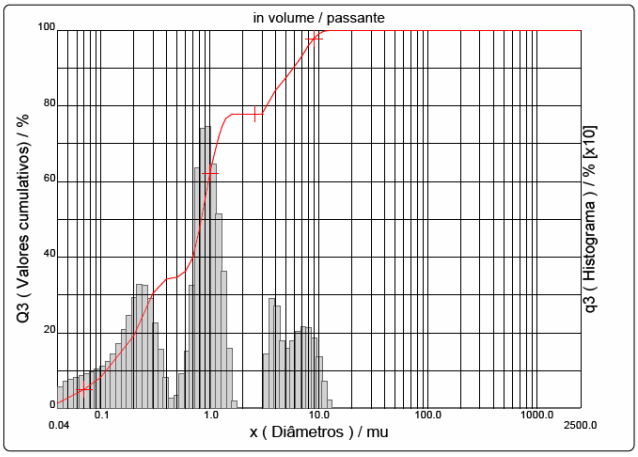


**Figure 4. Particle size distribution of WC-10wt.% Co powder milled at 300h**

The figure 5 show the variation of mean diameter of the composite powder milled at different times. The same figure shows that the milling time caused a reduction of the mean diameter of the particles. The composite powder milled at 300h have a mean diameter major than milled at 200h, this effect is caused by a cold welding between particles. The table 1 shows the variation of mean diameter of the particles in composites powders at milling time increase.

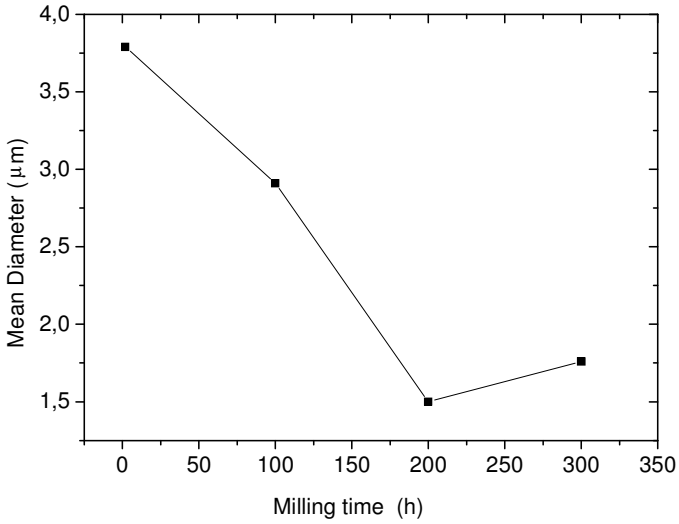


**Figure 5. Variation of mean diameter of the particles in composite powders milled at different times.**

**Table 1. Variation of mean diameter of the particles in composite powders milled at different times.**

| Milling time (h) | $D_{min}$ (μm) | $D_{max}$ (μm) | $D_{med}$ (μm) |
|---|---|---|---|
| 2 | 0,48 | 9,72 | 3,79 |
| 100 | 0,50 | 7,27 | 2.91 |
| 200 | 0,27 | 4,02 | 1,51 |
| 300 | 0,11 | 5,81 | 1,76 |

The theory of the crystalline systems establish the following axial relations: cubic system a = b = c and hexagonal system a = b ≠ c, R. A. Young (1965). In this context the figures 6 e 7 analyzing the axial relations "a" for the phases WC, Co-hcp and Co-fcc in WC-10wt.%Co composite.

In the composite powders the cells parameters for the phases WC, Co-hcp and Co-fcc decrease at milling time increase as show in figure 6. This decreasing is directly influenced for particle size reduction at milling time increase. This reduction caused the micro deformation in crystalline structure and decreasing crystallite size.

In the sintered composite the cells parameters for the phases WC, Co-hcp and Co-fcc are practically constant at milling time increase as show in figure 7. The variation existing in thousandth order it must be related with the formation of the substitutional solid solution during the sintering, influenced directly with the particle size reduction. At milling time increase caused allotropic transformations in Co phase, Y. Huang, et al (1994). The table 2 and 3 shows the cells parameters measurement of the composite powders and sintered composites, axial relations "a".

**Table 2. Cells parameters measurements of the composite powders, axial relations "a".**

| Milling time | Cells parameters (Å) | | |
|---|---|---|---|
| | WC | Co-hcp | Co-fcc |
| Start mat. | 2,900 | 2,5060 | 3,440 |
| Mec. mix. | 2,9064 | 2,5194 | ---- |
| 2h | 2,9064 | 2,5113 | 3,556 |
| 100 | 2,9057 | 2,4951 | 3,537 |
| 200h | 2,9040 | 2,4951 | --- |
| 300h | 2,9031 | --- | 3,506 |

**Table 3. Cells parameters measurement of the sintered composite, axial relations "a"**

| Milling time | Cells parameters (Å) | | |
|---|---|---|---|
| | WC | Co-hcp | Co-fcc |
| Start mat. | 2,900 | 2,506 | 3,544 |
| Mec. mix. | 2,907 | 2,528 | 3,857 |
| 2h | 2,909 | 2,532 | 3,852 |
| 100 | 2,906 | 2,508 | 3,859 |
| 200h | 2,909 | 2,524 | 3,868 |
| 300h | 2,968 | ---- | ---- |

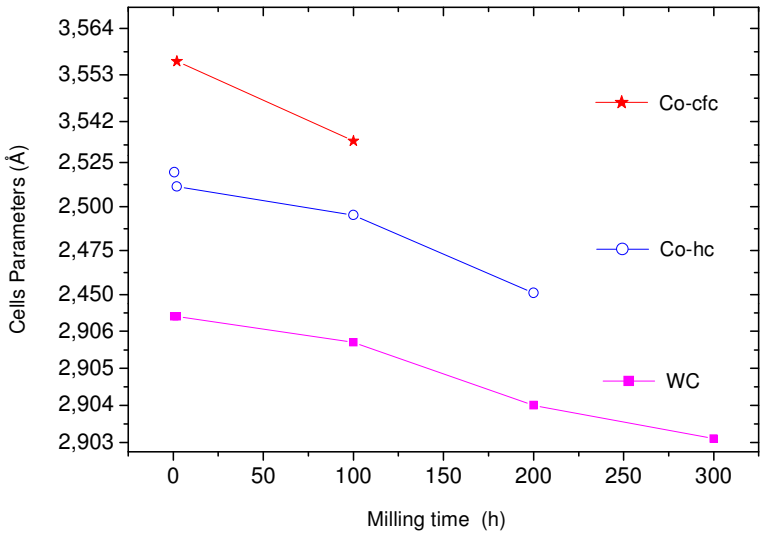


**Figure 6. Variation of the cells parameters versus milling time the phases WC, Co-hcp and Co-fcc in composites powders.**

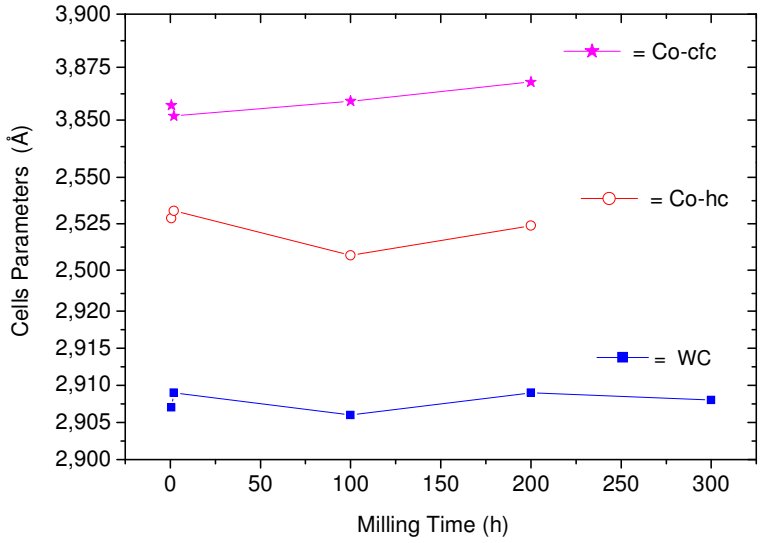


**Figure 7. Variation of the cells parameters versus milling time the phases WC, Co-hcp and Co-fcc in composites sintered.**

In the figures 8 and 9 are analyzing the axial relations “c” for the phases WC, Co-hcp following the theory of crystalline system.

At milling time increase the cells parameters in WC-10wt.%Co composite powders for the WC and Co-hcp phases increase until milled at 2 hours compared with starts materials, after 2 hours at milled until 300 hours decrease as show in figure 8.

The table 4 and 5 shows the cells parameters measurement of the composite powders and sintered composites, axial relations “c”.

**Table 4. Cells parameters measurements of the composite powders, axial relations "c".**

| Milling time | Cells parameters (Å) | |
|---|---|---|
| | WC | Co-hcp |
| Start mat. | 2,900 | 2,5060 |
| Mec. mix. | 2,9064 | 2,5194 |
| 2h | 2,9064 | 2,513 |
| 100 | 2,9057 | 2,4951 |
| 200h | 2,9040 | 2,4951 |
| 300h | 2,9031 | ---- |

**Table 5. Cells parameters measurement of the sintered composite, axial relations "c"**

| Milling time | Cells parameters (Å) | |
|---|---|---|
| | WC | Co-hcp |
| Start mat. | 2,900 | 4,206 |
| Mec. mix. | 2,841 | 4,210 |
| 2h | 2,843 | 4,209 |
| 100h | 2,839 | 4,197 |
| 200h | 2,844 | 4,211 |
| 300h | 2,842 | ---- |

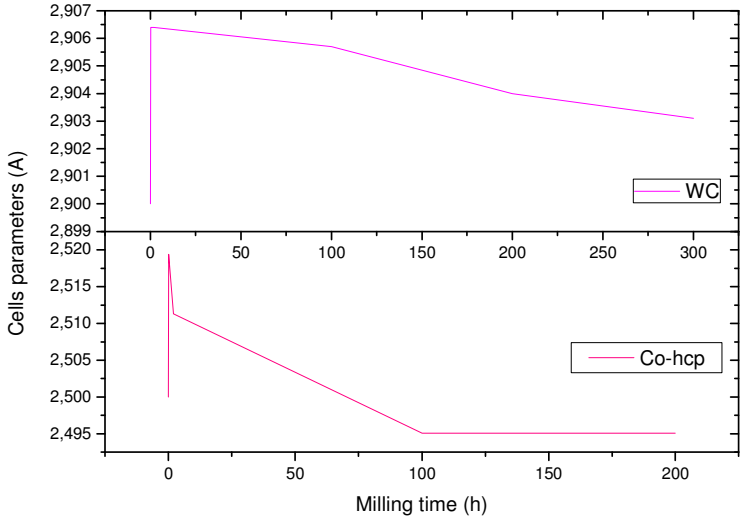


**Figure 8. Variation of the cells parameters versus milling time the phases WC and Co-hcp in composites powders.**

This decreasing is directly influenced for particle size reduction at milling time increase. This reduction caused the micro deformation in crystalline structure and decreasing crystallite size.

At milling time increase the cells parameters in WC-10wt.%Co sintered composite for the WC phase decrease until milled at 300 hours compared with starts materials. The cells parameters of the Co-hcp phase until milled at 2 hours increase compared with starts materials, after 2 hours at milled until 100 hours decrease. After 100 hours at milled until 200 hours decrease The variation existing in thousandth order it must be related with the formation of the substitutional solid solution during the sintering, influenced directly with the particle size reduction.

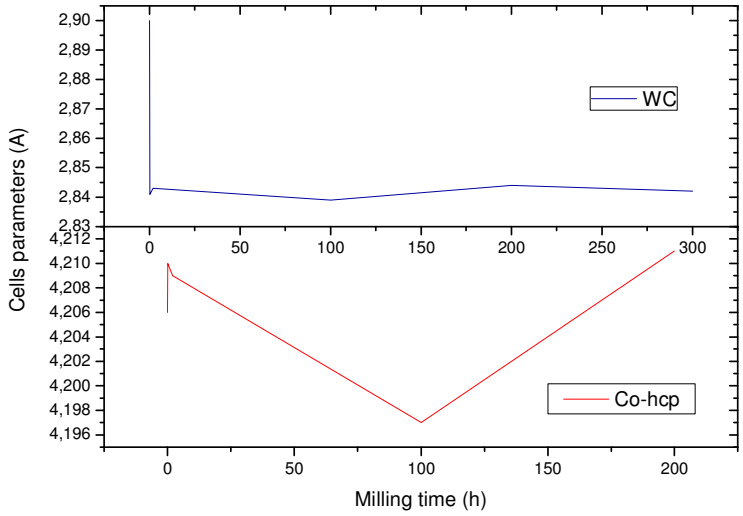


**Figure 9. Variation of the Cells parameters versus milling time the phases WC, and Co-hcp in composites sintered.**

## 4.0 CONCLUSION

The milling time caused a particle size reduction and mean diameter reduction. In the composite powder the cells parameters of the phases WC, Co-hc, Co-cfc decreasing at milling time increase. This decreasing is directly influenced for particle size reduction at milling time increase in axial relations “a”. This reduction caused the micro deformation in crystalline structure and decreasing crystallite size.

For the composites sintered the cells parameters of the phases WC, Co-hcp and Co-fcc it is practically constant in axial relations “a” The variation existing in thousandth order it must be related with the formation of the substitutional solid solution during the sintering, influenced directly with the particle size reduction.

In the WC-10wt.%Co composite powders for the WC and Co-hcp phases increase until milled at 2 hours compared with starts materials, after 2 hours at milled until 300 hours decrease in axial relations “c”. This variation is directly influenced for particle size reduction at milling time increase.

At milling time increase the cells parameters in WC-10wt.%Co sintered composite for the WC phase decrease until milled at 300 hours compared with starts materials. The cells parameters of the Co-hcp phase until milled at 2 hours increase compared with starts materials, after 2 hours at milled until 100 hours decrease. After 100 hours at milled until 200 hours decrease in axial relations “c”. These variations are related with the formation of the substitutional solid solution during the sintering, influenced directly with the particle size reduction.

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