INFLUENCE OF THE MILLING TIME IN THE MICROSTRUCTURAL PARAMETERS OF Ta2O5-Al POWDER REFINED BY RIETVELD METHOD

*R. A. Brito1, M. W. D. Mendes1, F. A. da Costa2, U. U. Gomes2, I. O. Nascimento1, C. Alves Jr1

1UFRN - Laboratório de Processamento de Materiais por Plasma, Campus Universitário, 59072-970, Natal-RN, Brasil. 
2 UFRN – DFTE, Laboratório de Materiais Cerâmicos e Metais Especiais, Natal, RN, Brasil
*roseaneab@gmail.com

ABSTRACT

Mechanical alloying (MA) is a solid-state powder processing technique involving repeated welding, fracturing, and re-welding of powder particles in a high-energy mill. This process is used for producing of fine powders containing unique microstructures. The process starts with mixing of the powders in the desired proportion. Then, the mixture is milled using the established time in the high-energy mill. The powder particles are submitted to repeated cycles of cold working and fracture, and the final product correspond to a composite powder, containing characteristics different of the initial constituents. Ta2O5-Al powders were milled in a planetary ball mill for different times in order to evaluate the influence of the milling time in their microstructural parameters like crystallite size and microdeformation. The microstructural parameters were obtained by the Rietveld Method. The results showed that the microstructural parameters were influenced by the increase of the milling time.

Key-words: High-energy mill, Tantalum Pentoxide, Aluminum, Rietveld Method.

INTRODUCTION

The high-energy mill has been used to producing a wide range of powders for several applications in the industry, including amorphous materials, intermetallic compounds, and solid solution alloys1-3. In this technique ductile–ductile, ductile–brittle, and brittle–brittle powder mixtures are milled to produce novel alloys4.

The process starts with mixing of the powders in the right proportion (typically, a blend of elemental or pre-alloyed powders) and loading the powder mix into the high-energy mill along with the grinding medium (generally steel balls). This mix is milled for the required time, in order to obtain powders with a smaller particle size, and to achieve a steady state between the fracturing and cold welding of the powder particles. The particle size decreases exponentially with time and reaches a small
value of a few microns only after a few minutes of milling. The level of contamination increases and some undesirable phases form if the powder is milled for times longer than required\(^5\).

Powders used in aluminothermic reactions of Ta\(_2\)O\(_5\)-Al mixtures require a previous preparation using high-energy milling, in order to promote the perfect contact between the phases (Al and Ta\(_2\)O\(_5\)), and, thus, the reaction can propagates for the whole volume of the powder\(^6,7\). The ductile Al particles are deformed, getting the shape of plates. The Ta\(_2\)O\(_5\) flakes are fragmented and the smaller hard fragments are embedded in the ductile aluminum by the collisions. As milling continues, different Al plates weld and break successively\(^8-10\). The final result is the formation of particles in which tantalum oxide fine particles are dispersed in a lamellar Al matrix\(^11\).

In this work a planetary ball mill was used for conducting the metal alloying experiments, in which ten grams of the mixture Ta\(_2\)O\(_5\)-Al were milled for 0, 2, 4, 6 and 10 hours. An excess of 5 wt.% Al with regard to the stoichiometric quantities was used to guarantee the appropriated mixture of the powders. After the stage of milling, the samples were characterized by SEM (using a Philips XL 30 ESEM), laser granulometry (in a CILAS, model 920L) and XRD (in a Shimadzu Diffractometer, using Cu K-\(\alpha\) radiation, with \(2\theta\) varying between 10 and 80º and scattering velocity of 2°.min\(^{-1}\)). The data obtained in the XRD analysis were refined by Rietveld Method in order to obtain the microstructural parameters like crystallite size and lattice strain.

**EXPERIMENTAL PROCEDURE**

A mixture of tantalum oxide (99.98%) and aluminum (99.86%) powders was used to carry out the milling tests. Ta\(_2\)O\(_5\) particles tend to agglomerate, forming flakes, while Al particles are constituted by irregular and compact grains, Fig. 1. The mean particle size determined by laser scattering for Ta\(_2\)O\(_5\) and Al was 0.8 µm and 5.2 µm, respectively.

Normally, about 10–15% stoichiometric excess of the reductant element is used to prepare the mixtures\(^5\). This excess reductant is used partly to compensate for the surface oxidation of the reactive reductant powder particles, e.g., Al\(^12\). In previous works, mixtures of Ta\(_2\)O\(_5\)-Al were studied and it was observed that stoichiometric mixtures did not present the same reactivity than that overstoichiometric in posterior processing, for example in aluminothermic reduction process\(^6,7\).
In this work, Al and Ta$_2$O$_5$ powder mixtures were prepared, using 10 g of Ta$_2$O$_5$ and 2.14 g of Al. This corresponds to an excess of 5 wt.% Al with regard to the stoichiometric quantities. The samples were mixed using a high energy planetary Fritsch Puleverisetti 7 mill for 0, 2, 4, 6 and 10 hours. It was used hardmetal balls (diameter: 15 mm; total mass: 100 g) and the milling speed was 400 rpm. The sample without milling (0 h) was hand mixed for 15 minutes to compare with that milled in the high-energy mill. A ball-to-powder weight ratio (BPR) of 1:10 was used to accomplish the tests.

After milling, the samples were characterized by SEM (using a Philips XL 30 ESEM), laser granulometry (in a CILAS, model 920L) and XRD (in a Shimadzu Diffractometer, using Cu K-α radiation, with 2θ varying between 10 and 80º and scattering velocity of 2°.min$^{-1}$). The data obtained in the XRD analysis were refined by Rietveld Method in order to obtain the microstructural parameters like crystallite size and the lattice strain.

RESULTS AND DISCUSSION

After the milling for whole the employed times, the particle size distribution presented three curves. Fig. 2 shows the distribution of particle size to a Ta$_2$O$_5$-Al powder, containing an excess of 5 wt.% Al and milled for 6 h.

The size distribution of the milled powder is trimodal. The different ranges of size are attributed to the absence of dispersion or homogeneity of the phases during the milling. Thus, three kinds of different particles can be found in the powder. The ranges containing finer particle size correspond to the original particles of Ta$_2$O$_5$ and Al, while, the range with higher particle size is related to the composite particles of Ta$_2$O$_5$-Al formed during the milling process.

XRD patterns to the mixtures Ta$_2$O$_5$-Al are shown in Fig. 3, where is presented the effect of the milling time in the microstructural characteristics of the powders prepared by mechanic mixture and milling. Broadening of the peaks of Ta$_2$O$_5$ and Al is observed with the milling time. These effects are related to the strain (distortion) of the crystalline lattice and decrease of the crystallite size caused by the high energy of the ball-powder-ball collisions. In extreme milling intensity, the phases can be become completely amorphous.

High energy milling causes strain of the crystal lattice, deformation of the ductile phases, cold welding of the particles and fracture of the brittle phases. The ductile Al
particles are deformed, getting the shape of plates. The Ta₂O₅ flakes are fragmented and the smaller hard fragments are embedded in the ductile Al by the collisions. As milling continues, different Al plates weld and break successively⁹⁻¹³. The final result is the formation of composite particles of tantalum oxide and Al⁸⁻⁹.

The crystallite size and lattice stain of Ta₂O₅-Al powder is calculated from the peak broadening methods. The Rietveld method was used to calculate the crystallite size and the lattice strain of the powders prepared by high-energy mill for 0, 2, 4, 6 and 10 h. The variation of the crystallite size and lattice strain is shown in Fig. 4 (A) and (B). In Fig. 4 (A) it can be observed that the crystallite size decreases with the milling time. Both the phases, Ta₂O₅ and Al present the same behavior, although, values of crystallite size to Al is higher, compared to the Ta₂O₅ values. In the case of Ta₂O₅ the values become apparently constant for 2, 4 and 6 h of milling.

The lattice strain increases with the milling time, Fig. 4 (B). In this case, the values of the lattice strain to the Ta₂O₅ are higher. Values for the mean crystallite size were calculated using the Scherrer formula, and for the lattice strain, using the Williamson-Hall formula.

Secondary electron micrographs of milled powders are shown in Fig. 5. Fig. 5 (A) shows the Ta₂O₅-Al powder mechanically mixed (0h). In this powders, fine particles of Ta₂O₅ are dispersed onto large particles of Al, and the different components can be observed separately. This mechanic mixture is not efficient to be used in the aluminothermic reaction of these powders, since the Al phase is not in an enough contact with the flakes of Ta₂O₅, and the reaction don’t propagates for the whole volume of material.

During the initial stages of the milling process, the powder particles are flattened and cold-welded together leading to an increase in the particle size, Fig. 5 (B). The increase of the particle size during initial hours of milling indicates dominance of cold welding process over fracture. Increasing the milling time, fracture dominates, resulting in reduction of particle size. It can be observed in powders milled for 4 and 6 h, Fig. 5 (C) and (D). Milling of the powder blends up to 10 h results in particle size reduction and an increase in the chemical homogeneity of the powders (Fig. 5(E)). Fig. 5 (F) shows the powder milled for 10 h in the back scattering mode, where is possible to observe that the structure of this powder consist in higher composite particles containing fine particles dispersed onto their surface. Differences of color contrast is not observed in these particles, thus, the particles probably present the
same chemical composition.

The use of the milling process is very important before the aluminothermic reduction because this process promotes the contact between the present phases, contributing to the propagation of the reaction. In results obtained by Brito\textsuperscript{6, 7}, the efficiency of the aluminothermic reaction was higher observed in samples milled for 6 and 10 h.

CONCLUSIONS

It was observed that the crystallite size decrease with the milling time, and the lattice strain increase with the milling time, for the two phases studied. When these powders are submitted to a high-energy milling, during the initial stages of the milling, the particles are flattened and cold-welded together leading to an increase in the particle size, but, with the milling time, occurs dominance of cold welding process over fracture, until the fracture dominates, resulting in reduction of particle size.

ACKNOWLEDGMENTS

The authors are grateful to CNPQ and CAPES for the financial support.

References


Figure captions:

Figure 1 – Fine flakes of Ta₂O₅ particles (A) and Al particles (B).

Figure 2 – Particle size distribution for a powder Ta₂O₅-Al milled for 6 h.

Figure 3 - XRD patterns of the Ta₂O₅-Al powders milled during 0, 2, 4, 6 and 10 h. Only peaks of Ta₂O₅ and Al are present.

Figure 4 – Variation of crystallite size and lattice strain of Ta₂O₅ (A) and Al (B) powders with the milling time.

Figure 5 – Evolution of the powder morphology with the milling time. (A)Mechanic mixture (0h); Samples milled for (B) 2h; (C) 4h; (D) 6h and (D) 10 h.
Figures:

Figure 1: R. A. Brito, M. W. D. Mendes, F. A. da Costa, U. U. Gomes, I. O. Nascimento, C. Alves Jr.
Figure 2: R. A. Brito, M. W. D. Mendes, F. A. da Costa, U. U. Gomes, I. O. Nascimento, C. Alves Jr.

Figure 3: R. A. Brito, M. W. D. Mendes, F. A. da Costa, U. U. Gomes, I. O. Nascimento, C. Alves Jr.
Figure 4: R. A. Brito, M. W. D. Mendes, F. A. da Costa, U. U. Gomes, I. O. Nascimento, C. Alves Jr.
Figure 5: R. A. Brito, M. W. D. Mendes, F. A. da Costa, U. U. Gomes, I. O. Nascimento, C. Alves Jr.