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COMPARATIVE STUDY OF Al-Ni-Mo ALLOYS OBTAINED BY MECHANICAL ALLOYING IN DIFFERENT BALL MILLS

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Abstract. A comparative study was carried out for an alloy of $Al_{50}(Ni_{75}Mo_{25})_{50}$ processed by two different high energy ball mills. A SPEX and Simoloyer mill were used. The milled products were characterized using X-Ray Diffraction and Scanning Electron Microscopy. A different morphology and microstructural evolution were found with each mill used. It was evident that prolonged milling time induced the formation of two different intermetallic compounds (AlNi or $AlMo_3$). Furthermore, the milling intensity had an important effect on its microstructural evolution and phase formation sequence.

1. INTRODUCTION

Some transition metals have been used as precursor materials for catalysts preparation. In petrochemical industries, the objective of many researchers has been to optimize the refinement of crude oil. Ni and Mo-based catalysts have proved to have excellent catalytic activity [1,2]. Bimetallic Ni-Mo catalysts can be produced by different techniques. One of these techniques is Mechanical Alloying (MA). Through MA, it is possible to produce metastable, nanocrystalline, and novel materials. However, one of the main problems with this kind of catalyst is the low surface area (SA) values in milled products. Through chemical methods, it is possible to increase the SA in milled products by adding Al and then by its subsequent removal. Nevertheless, the influence of milling parameters has not been properly investigated and these variables have an important effect on microstructural evolution during milling and should be considered to explain the novel properties of the final products. In this work, we studied the effect of mill type and milling time to understand the microstructural evolution of an Al-Ni-Mo alloy processed by MA. A SPEX and a Simolyer high energy mill were used in this study. The Simoloyer mill uses a horizontally borne rotor which allows the transfer of the kinetic energy of ball impacts into the sample with a collision velocity of 14 ms^{-1} [3]. In SPEX mills, the balls and powder are placed in a vial which is agitated in complex 3D cycles at high frequency and with an average impact velocity of 4.2 ms^{-1} [4]. While other methods exist for producing catalysts for hydrodesulfization, we focused on doing it through MA. For this reason we chose the alloy Al-Ni-Mo for this work [5,6].

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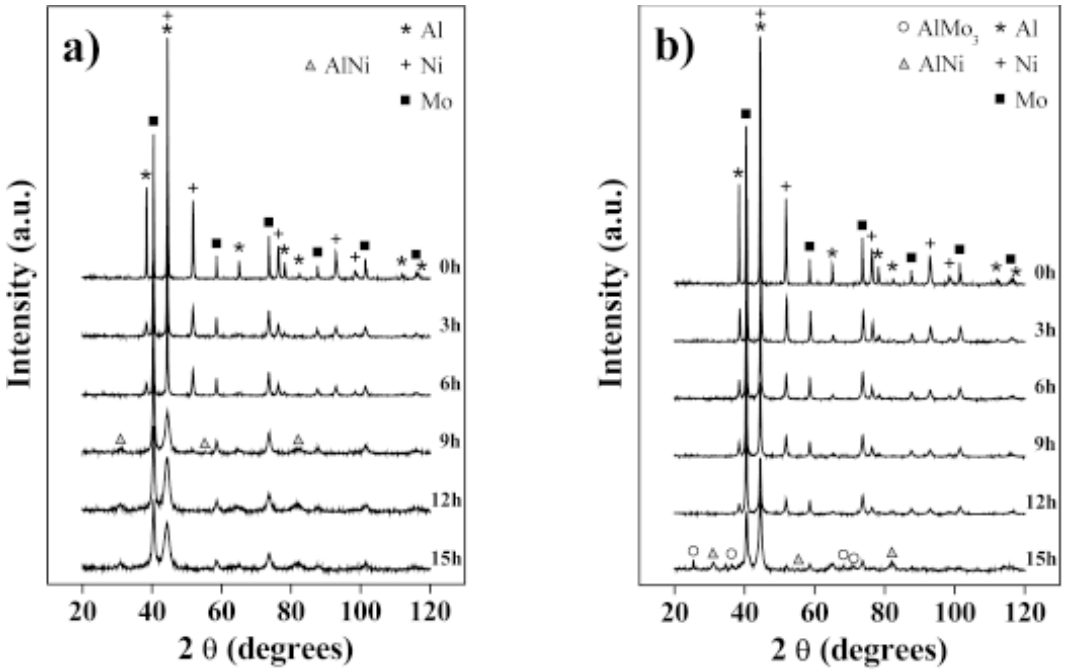

Fig. 1. XRD spectra from powders milled with different time intervals, a) - powders processed in SPEX mill, b) - powders processed in Simoloyer mill.

2. EXPERIMENTAL DETAILS

Ni, Mo, and Al (99.5% pure, -200 mesh in size) powders were used as the raw materials. Nominal composition was set to an atomic percent of $Al_{50}(Ni_{75}Mo_{25})_{50.}$ SPEX and Simoloyer mills were used to process the powder mixtures. Milling time intervals were set to 0, 3, 6, 9, 12, and 15 h. The milling medium and devices used were made from hardened steel. A protective argon atmosphere was maintained during the milling process in both mills. The milled products were characterized using a diffractometer model Siemens D-5000 and operated with a Cu-Kα radiation of 0.154 nm and with a graphite monochromator. The milled products were also characterized by a scanning electron microscope (SEM) model JEOL JSM-5800LV supplied with an electron dispersion spectrometer (EDS).

3. RESULTS AND DISCUSSION

It is known that the higher the milling intensity, the shorter the milling time. Milling intensity (I) can be briefly described by the following equation:

$$I = f(k, m, V, P),$$

where k is the experimental coefficient and m the mass of the ball. V is the average velocity of the balls and P is the weight ratio of balls to powder [3]. Because of this, collision velocity is an important parameter for final milling intensity (if all other variables remain constant); consequently, the final milling intensity has an important effect on the structural refinement of the milled powder sample. These inputs (k, m, V, and P) have been related to the distribution and evolution of particle size [4].

X-ray Diffraction - The corresponding XRD patterns from the Al-Ni-Mo powder mixture milled in the SPEX and Simoloyer mills at different time intervals are shown in Figs. 1a and 1b. The 0-hour (0 h) spectrum corresponds to a mixed condition. As the milling time increased, the Al, Ni, and Mo peaks became weaker and widened. Furthermore, in the SPEX milled products, and by judging the slight displacement of the Ni diffraction peaks towards higher 2θ values (9 –15 h), the formation of a solid solution might be predictable. After 9 h of processing, the Al peaks disappear completely. Moreover, within 12 h a new phase emerged (crystallized), and was identified as the cubic AlNi intermetallic compound. This phase grew in relation to

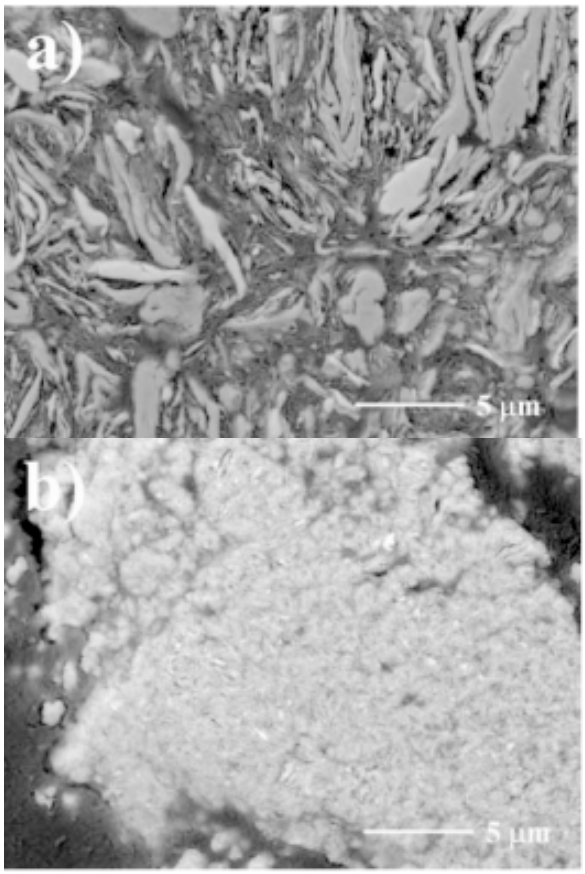

Fig. 2. SEM micrographs in samples processed in SPEX mill with different time intervals, (a) 3 h and (b) 12 h.

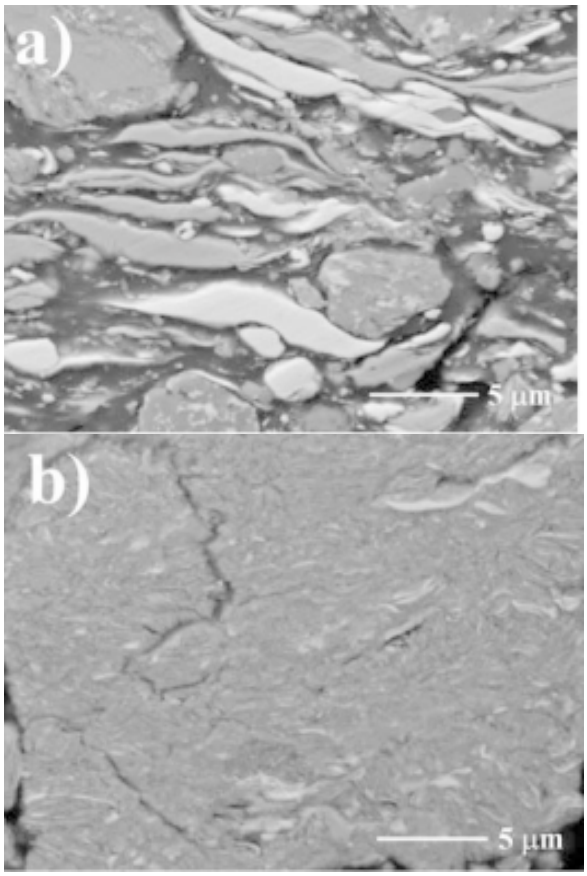

Fig. 3. SEM micrographs in samples milled in Simoloyer with different time intervals, (a) 3 h and (b) 12 h.

milling time. No evidence of other phases was obtained. In the XRD patterns of the milled powders from SPEX (Fig. 1a), it is clear that the Mo diffraction peaks shortened and widened without any position shifting. This could indicate that the Mo was not dissolving the Ni, Al, or Fe (due to the wear and tear of the milling medium). This result was expected considering the insolubility of Ni, Al, or Fe in the Mo, and has been reported [7]. The powders processed by the Simoloyer mill (Fig. 1b) presented a similar microstructural behavior with short milling time. After 3 h of processing, all the peaks presented a small shift to higher 2θ values; denoting a decrease in the lattice parameter. However, as the milling time was increased, the peaks returned to their original position. These variations in the lattice parameter during MA processing can be produced by the increasing the vacancy density and by subsequently relaxing them. These phenomena have already been reported [8]. The Simoloyer samples also showed the presence of two new phases. XRD spectrometry revealed the formation of $AlMo_3$ and AlNi intermetallic compounds after long milling times (12-15 h). Different results were observed using different kinds of mills. These differences were directly correlated with the milling intensity of each mill.

Scanning Electron Microscopy - After 3 h of milling time a lamellar structure in the processed powders of both mills was evident (Figs. 2a and 3a). The lamellar structure was formed by a gray phase and a bright phase. EDS analyses showed the presence of Al and Ni in the gray phase and almost pure Mo in the bright phase. With longer milling time (>9 h), a highly homogeneous microstructure was evident in the SPEX powders (Fig. 2b). By contrast, undissolved Mo (bright phase)

remained in the powders processed by the Simoloyer mill (Fig. 3b).

4. CONCLUSIONS

Different morphologies and microstructural evolutions were found for powders processed by SPEX and Simoloyer mills. Longer milling times brought about the formation of two different intermetallic compounds. The milling intensity had an important effect on the microstructural evolution and phase formation sequence.

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