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NANOCRYSTALLINE Al-Mn MASTER ALLOYS OBTAINED BY MECHANICAL ALLOYING

Adina UŞURELU-CRISTEA[1], Gabriela POPESCU[2], Mihai BUZATU[3], Roxana TRUŞCĂ[4]

În lucrare sunt prezentate cercetările experimentale pentru obținerea unor prealiaje Al-Mn cu structură nanocristalină. Pulberile inițiale de Al si Mn au fost aliate mecanic intr-o moară planetară de mare energie tip RETSCH PM400. Amestecurile de pulberi au fost măcinate atât în mediul uscat cât şi umed, la diferite ore de măcinare. Rezultatele experimentale au fost analizate prin analiză SEM, EDS şi difracție de raze X. Experimentele au arătat că se pot obține prealiaje Al-Mn cu structură nanocristalină prin tehnica folosită.

The paper presents experimental research to obtain Al-Mn master alloys with nanocrystalline structure. The initial powders of Al and Mn were mechanically alloyed in a planetary high energy mill type RETSCH PM400. Mixed powders were milled in both dry and wet milling medium at different times. The experimental results were analyzed by SEM, EDS and X-ray diffraction analysis. Experiments have shown that it can be obtained nanocristaline Al-Mn master alloys using this technique.

Keywords: mechanical alloying, composites, powder, characterization

1. Introduction

Mechanical alloying is a complex process involving a large number of variables optimized to achieve the desired product phases and to obtain the desired structure: mill type, milling chamber, milling speed, type, and size of grinding materials, ball-material weight ratio, the degree of filling of the milling chamber, milling atmosphere, process control agents, milling temperature. [1]

By using mechanical alloying (MA) complex high performance materials can be obtained to meet the demands of today's modern industry. Mechanical alloying of metal powders allows obtaining composites, which are very difficult or even impossible to to be obtained by other methods. Mechanical alloying can

[1] PhD student, Materials Science and Engineering Faculty, University POLITEHNICA of Bucharest, Romania, e-mail: usurelu.cristea.adina@gmail.com
[2] Prof., Materials Science and Engineering Faculty, University POLITEHNICA of Bucharest, Romania, e-mail: gabriela.popescu@.upb.ro
[3] Prof., Materials Science and Engineering Faculty, University POLITEHNICA of Bucharest, Romania, e-mail: buzatu.mihai@yahoo.com
[4] PhD Eng. S.C. METAV R&D S.A., Bucharest, Romania, e-mail: truscaroxana@yahoo.com

achieve amorphous phases, intermetallic compounds at room temperature, nanocrystalline powders, metal alloy immiscible or synthesis of carbides or nitrides at low temperatures. Mechanical alloying goal is to reduce particle size, change shape and mixing or homogenization of powders. This happens through repeated breaking and rewelding of powder particles mixture in a high energy ball mill. Strong deformation of the particles leads to the hardening of surface layer surface layer which is crushed and scattered, allowing the homogenization of mechanically alloyed mixture.

MA process is strongly dependent on the chemical reactivity of powders subjected to elementary milling, the milling environment (in air or inert gas), the chemical composition and the initial state of powders, powder components and the intensity and duration of milling and as a result, mechanical alloying produces homogeneous mixtures of crystalline and amorphous phases. [2].

Allotropic states of manganese are: α, β, γ and δ, each being able to dissolve the aluminum. The α-Mn is stable at room temperature, and α and β phases are complex cubic crystal structure [3, 4]. Magnetic properties of Al-Mn alloys are ferromagnetic metastable tetragonal τ phase due to the body centered lattice, which can be obtained by different methods over a limited composition range. The $\varepsilon \rightarrow \tau$ transformation occurs by different mechanisms depending on the microstructure and composition of the initial ε phase. Ferromagnetic properties depend strongly on the τ phase thermodynamic treatment and structure.

McAlister and Murray [5] indicated that the composition of the ε phase was 53.16 to 59.56% at.Mn. Liu [6] and others have shown that this area is 54.4 to 71.3% at. Mn, and that ε phase transformation occurs at compositions less than 58% at. Mn resulting in a ferromagnetic τ phase, while the ε phase with greater composition than 58% at. Mn change in β-Mn phase.

Muller [7] and colleagues have demonstrated, based on DTA data, the existence of ε phase extended to lower temperatures, where the eutectic temperature is 777^0C instead of 857^0C. Several efforts were made by Ibrahim et al. to investigate the possibility for obtaining τ phase using mechanical alloying technique. The initial composition used by them was 70% Mn.

This paper presents the obtaining and characterization of two compositions of Al-Mn master alloys, with 65% and 75% Mn.

2. Experimental conditions

The materials used in the experiments were fine powders of Mn (99.3%) and Al (99.5%) with grain sizes of 44 μm. The size of elementary initial powders was micrometric aiming to obtain grains in the nanometer scale, that can be highlighted using X-ray diffraction and scanning electron microscopy. Mixing and milling were made in a high energy planetary mill type RETSCH PM 400 (Figure 1).

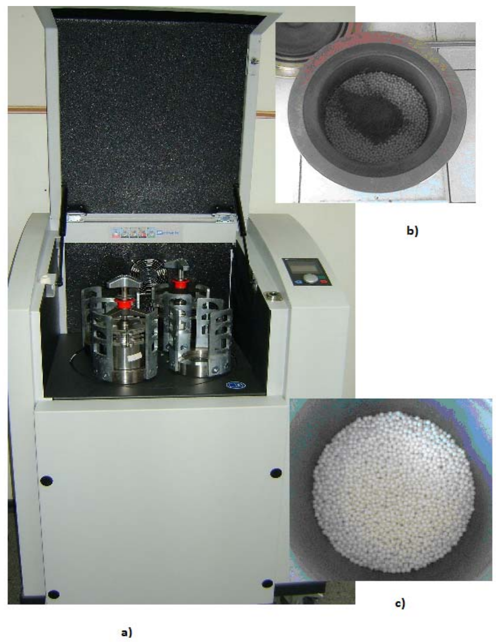


Fig. 1: a) RETSCH Planetary Mill PM 400 and milling chamber, b) milling vial, c) grinding balls

By using mechanical alloying technique in dry or wet environment Al-Mn master alloys with nanocrystalline structure were obtained. During the experiments the Mn content was varied resulting in two master alloys presented in Table 1.

Table 1

Compositions used in the experimental

% gr. Mn	% gr. Al
65	35
75	25

The working parameters were:
- Milling time - 5 hours
- Rotational speed - 300 rpm,
- Ball-to-powder weight ratio - 10:1.

Grain size analysis of the obtained powder mixture revealed the formation of individual particles of powder agglomeration and compounds, which prevented obtaining meaningful results on particle size. Due to the agglomeration of powder particles by dry milling process the wet milling using toluene or petroleum ether as a milling medium was chosen.

Parameters used in wet milling are:

- Milling time - 3, 5, and 8 hours
- Rotational speed – 300 rpm,
- Ball-to-powder weight ratio - 10:1.

After the experiments performed for obtaining of nanocrystalline Al25%-Mn75% and Al35%-Mn65% master alloys, X-ray diffraction, SEM and EDS analysis have been used for characterization.

3. Results and discussion

Al and Mn initial powders used in the experiments with 44µm grain size, were investigated by scanning electron microscopy, SEM microstructures of these powders are presented in Figures 2 and 3. The images presented indicate slightly rounded shape of Al powder and sharp angles of the polyhedral Mn powder.

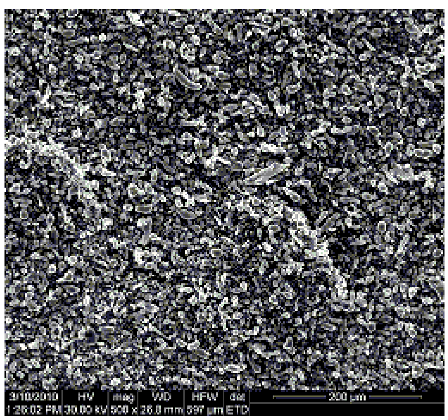


Fig. 2: SEM image of Al before grinding the powder

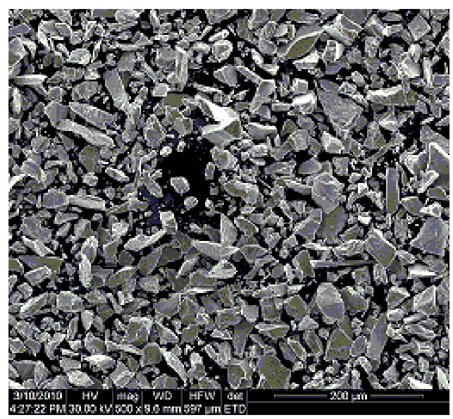


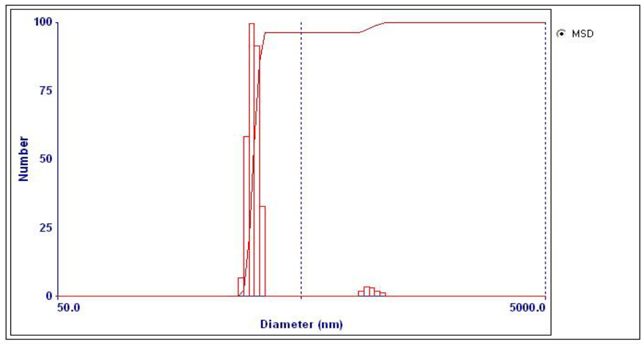
Fig. 3: SEM image of Mn before grinding the powder

Determination of particle size of the powder obtained after grinding was carried out by using Nanoparticle Size Analyser 90 Plus device, Brookhaven. This device is used to determine the size of nanoparticles on the principle of dynamic light scattering. Scattered light intensity fluctuations are analyzed by particles in Brownian motion to obtain a medium-sized and polidispersed or to obtain a complete distribution.

Measurements are made only for nanoparticles dispersed in liquid medium. Dimensional measurement interval is 1 nm ... 6 µm. Average diameter can be expressed by: light intensity, the number or volume of nanoparticles in suspension. For each type of powder three measurements were carried out. Particle size of Al35%-Mn65% and Mn75%-Al 25% powder are between 295.2 and 678.3 nm, but these measurements may be inaccurate due to particle agglomeration. Particle size analysis of Al35%-Mn65% and Mn75%-Al 25% samples milled for 5 hours are shown in Figures 4 and 5.

2.1-Mn65Al35 (Combined)

Effective Diameter: 678.3 nm
Polydispersity: 0.188
Avg. Count Rate: 2.8 Mcps
Baseline Index: 7.8
Elapsed Time: 00:01:30

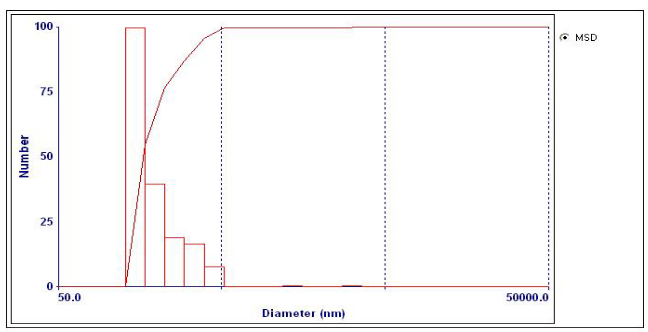


Run	Eff. Diam. (nm)	Half Width (nm)	Polydispersity	Baseline Index
1	617.8	283.8	0.211	0.9
2	687.9	219.1	0.101	8.9
3	731.6	361.5	0.244	8.2
Mean	679.1	288.1	0.186	6.0
Std. Error	33.2	41.2	0.043	2.6
Combined	678.3	294.4	0.188	7.8

Fig. 4: Particle size analysis of Al-65% Mn sample, 5 hours milling

3.1-Mn75Al25 (Combined)

Effective Diameter: 295.2 nm
Polydispersity: 0.005
Avg. Count Rate: 1.8 Mcps
Baseline Index: 4.7
Elapsed Time: 00:01:30



Run	Eff. Diam. (nm)	Half Width (nm)	Polydispersity	Baseline Index
1	296.2	20.9	0.005	8.4
2	302.7	73.6	0.059	0.0
3	289.9	20.5	0.005	7.4
Mean	296.2	38.3	0.023	5.2
Std. Error	3.7	17.6	0.018	2.6
Combined	295.2	20.9	0.005	4.7

Fig. 5: Particle size analysis of Al-75% Mn sample, 5 hours milling

Al-Mn samples have been investigated using a DRON 3 diffractometer under the following conditions: horizontal Bragg-Brentano goniometer; step-by-step recording with 0.1 increment, CuKα radiation (λ=0.1541nm), HV=35 kV; I=30 mA. The compounds formed in the Al-Mn powder were Al_8Mn_5 and $Al_{15}Mn_{11}$, as indicated in the diffractograms in figures 6 and 7.

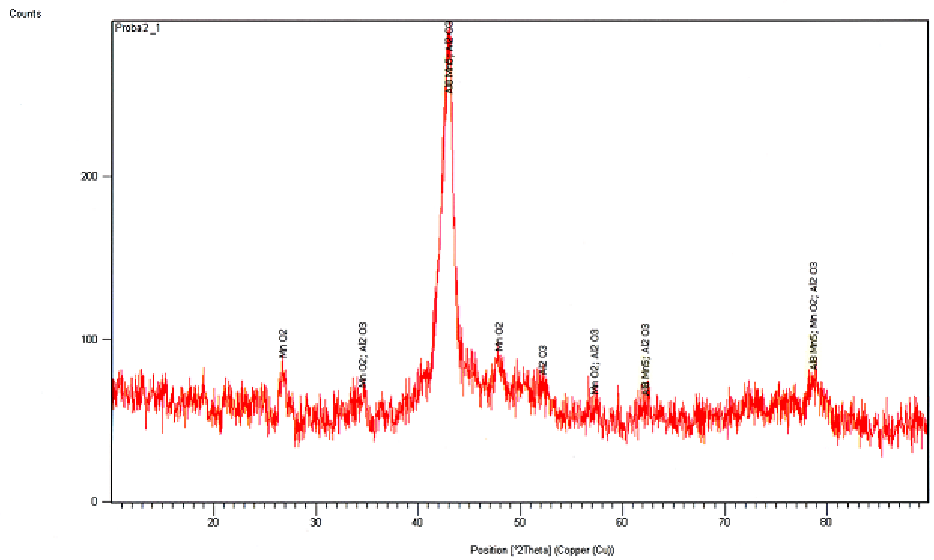


Fig. 6: Diffractogram of Al-65% Mn master alloy, 5 hours milling

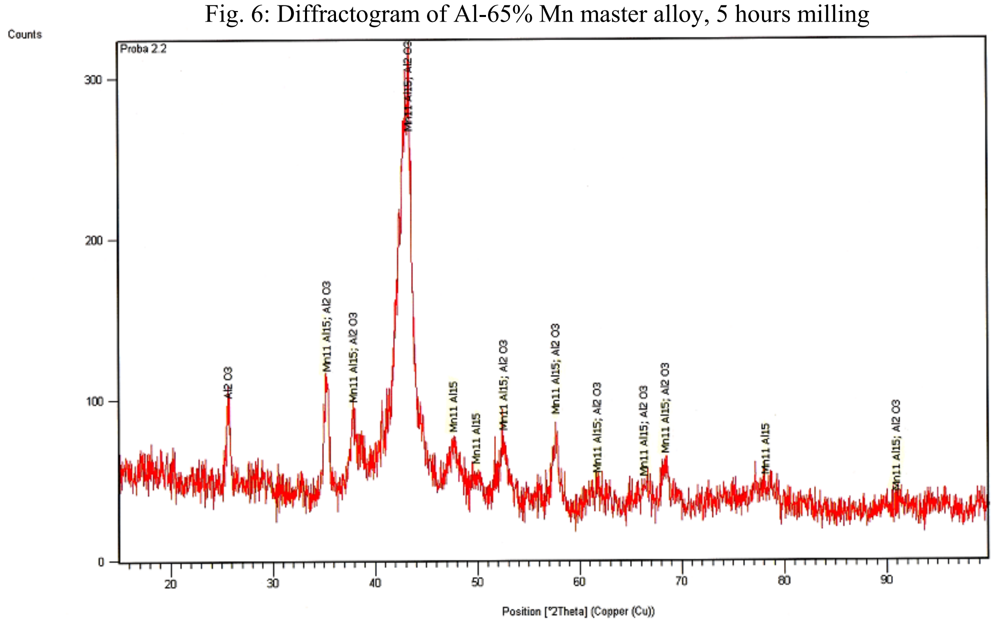


Fig. 7: Diffractogram of Al-75% Mn master alloy, 5 hours milling

The microstructures of alloyed powders were characterized by scanning electron microscopy, using QUANTA INSPECT F microscope equipped with EDS analyzer and X-ray diffractometer type Panalytical X' PERT MPD.

The size of powders compounds formed in the Al-75% Mn sample, milled for 3 hours, ranged from 19.0 to 34.4 nm and is shown in fig. 8.

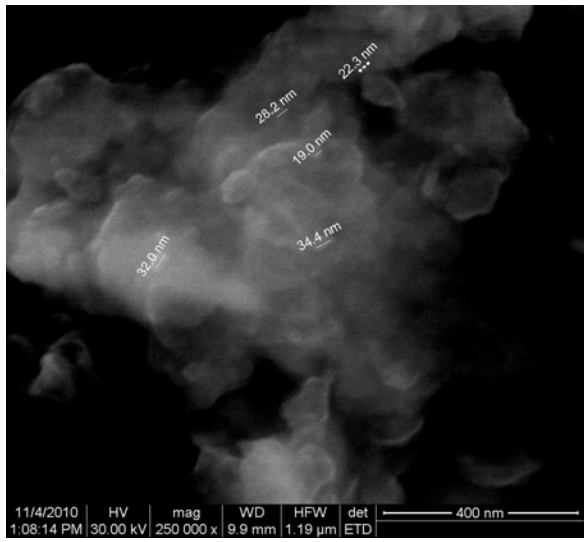


Fig. 8: SEM image of Al-75% Mn sample, 3 hours milling

EDS analysis of sample Al-75% Mn after 3 hours milling is shown in fig. 9 (X-ray emission spectrum in the corresponding SEM image in fig. 8).

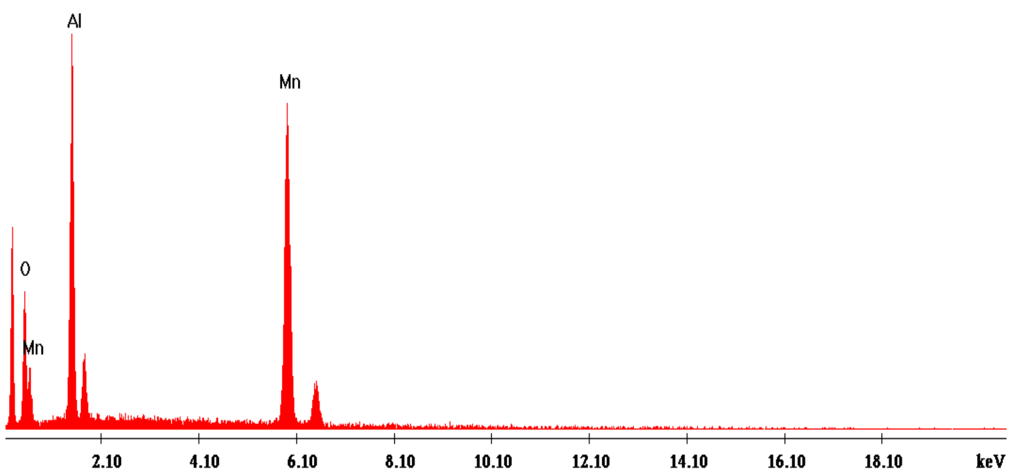


Fig. 9: EDS analysis of Al-Mn sample, 3 hours milling

In Al-75% Mn sample milled for 5 hours crystallite sizes ranging from 19.6 to 41.3 nm, were obtained as noted in fig. 10.

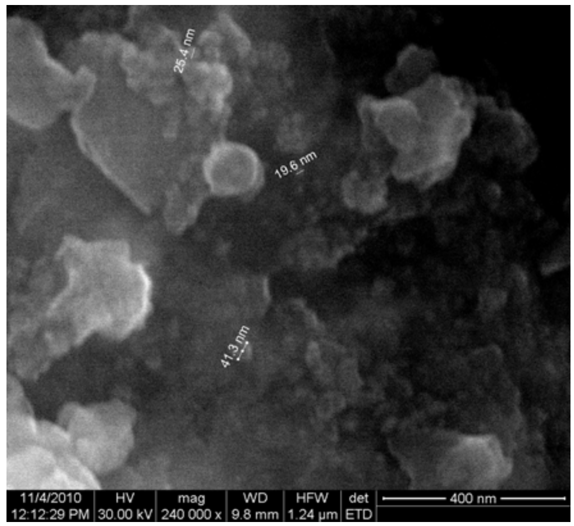


Fig. 10. SEM microstructure of Al-75% Mn sample, 5 hours milling

EDS analysis of Al-75% Mn sample milled for 5 hours is shown in fig. 11 (X-ray emission spectrum in the corresponding SEM image in fig. 10).

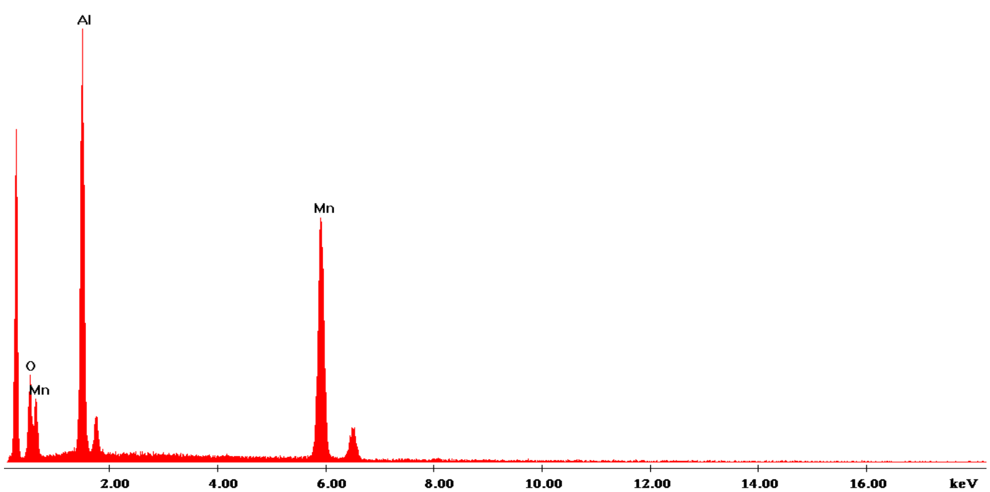


Fig. 11. EDS analysis of sample Al-Mn milling 5 hours

Al-75% Mn sample obtained after 8 hours milling have crystallite sizes ranging from 39.2 to 89.9 nm, as can be seen in figure 12.

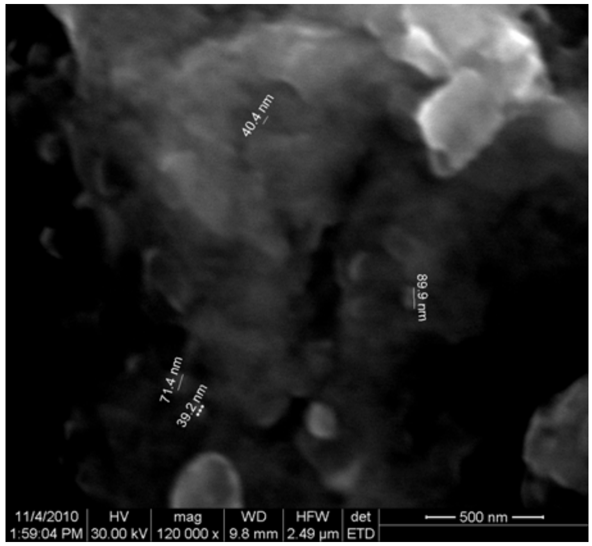


Fig. 12: SEM microstructure of Al-75% Mn sample, 8 hours milling

EDS analysis of Al-75% Mn sample milled for 8 hours is shown in fig. 13 (X-ray emission spectrum in the corresponding SEM image presented in fig. 12).

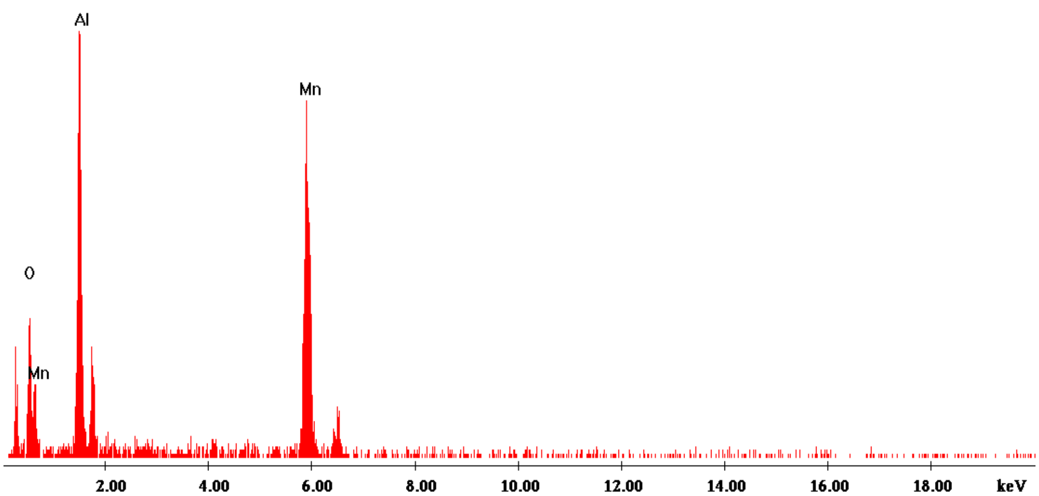


Fig. 13. EDS analysis of sample Al-Mn milling 8 hours

4. Conclusions

From the experiments performed until now, we can conclude the following:

- Two types of Al-Mn master alloys (Al35%-Mn65% and Al25%-Mn75%) with nanometer structure were obtained.
- Particle size distribution varies depending on milling time, crystallite reduction taking place with increasing duration of milling.
- Two intermetallic compounds were found that formed during the mechanical alloying process, namely Mn_5Al_8 and $Mn_{11}Al_{15}$.
- Milling in a dry environment of Al35%-Mn65% and Al25%-Mn75% master alloys led to agglomeration of powder particles.
- According to particle size analysis, Al35%-Mn65% and Al25%-Mn75% powders particle sizes were between 295.2 and 678.3 nm.
- Milling in wet environment led to better results crystallite sizes much smaller than those of samples obtained by milling in dry environment being obtained.
- Scanning electron microscopy reveals the nanometer size of the crystallites, measured particle sizes ranging from 19.0 to 34.4 nm for Al-75% Mn sample milled for 3 hours, 19.6 to 41.3 nm for Al-75% Mn sample milled for 5 hours, from 39.2 to 89.9 nm for Al-75% Mn sample milled for 8 hours.

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