SYNTHESIS OF NICKEL ALUMINIDES BY MECHANICAL ALLOYING IN BALL MILLS

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This paper is aimed at highlighting the effects of changing the mechanical alloying conditions in ball mills on the conversion rate of the Al-Ni powder mixture in the nickel aluminides, on their type and morphology of the newly-appeared particles. The effects of the variation of the energy released by the grinding bodies in the ball mills in operating, the ratio between the weight of the grinding bodies weight/weight of the material undergoing fragmentation/ mechanical alloying as well as their running time, on the type and proportion of the intermetallic compounds resulted from the Al-Ni system have been estimated and analyzed. It was concluded that, in respect of light-weight loads, the specific energy impact is low, therefore the increase of the mill's running time would not determine a significant change of the ratio of the synthesis products resulted from the interaction of components; upon the increase of the grinding bodies' weight and of the mills' working time, the effects on the conversion rate become significant.

Keywords: mechanical alloying, ball mills; nickel aluminides

1. Introduction

The nickel aluminides feature phases with high potential of increasing the working performance of light metal matrices or alloys. Among the five aluminides present in the system Al-Ni (Al3Ni2, Al3Ni5, Al3Ni, AlNi3, AlNi) [1], the last two are characterized by a particularly high thermodynamic stability at temperatures above 1000°C, associated with ductility, hardness, mechanical strength and strength to oxidation, carburization and nitriding [2]. The reactions involved in the formation of nickel aluminides stable at high temperatures are strongly viable from thermodynamically point of view ($\Delta G<0$) and their heat effect is noticeable ($\Delta H<0$) [3]

$Al+3Ni=AlNi_3$	ΔG^{873K}=-145.2.1 KJ/mol	ΔH^{873K} =-161.5 KJ/mol
	ΔG^{1273K}=-133.1 KJ/mol	ΔH^{1273K}=-175.1 KJ/mol
$Al+Ni=AlNi$	ΔG^{873K}=-112 KJ/mol	ΔH^{873K} =-128.8 KJ/mol
	ΔG^{1273K}=-101.9 KJ/mol	ΔH^{1273K}=-137.8 KJ/mol

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The nickel aluminides can be obtained by means of a variety of specific techniques or during the thermal or mechanical-thermal processing of the products containing the elements of interest: starting from casting, forging, rolling, extrusion, hot isostatic pressing, injection molding, pressure sintering and reaching the combustion synthesis by the two sub-versions (SHS - self-propagating high- temperature synthesis and VCS - volume combustion synthesis) or by the mechanical alloying [4, 5]; aliting of nickel matrices [6, 12] is also a method to synthesize the nickel aluminides. The techniques which are mainly applied to produce the nickel aluminides are those belonging to the group of combustion or mechanical alloying synthesis methods. Simultaneously, there is a variety of other process versions that have common features with each of the two groups mentioned above [7; 8; 9; 10; 11; 12]. The use of electricity to ensure the powder sintering within the techniques known as SPS (Spark Plasma Sintering) and CATS (Reactive current activated type-based sintering of nickel aluminides) generates a major activation of the sintering process's kinetics [13] and continuation of the nickel aluminides' synthesis process.

2. Materials and equipment used during the research

The powders used in the research (aluminum and nickel powders) were obtained by air spraying (aluminum powder made by Zlatna, Romania) or by Sherritt hydrometallurgical process (Alfa Aesar, Germany). The chemical compositions of aluminum and nickel powders are presented in Table 1 while the particles' morphology is highlighted in Fig. 1.

Table 1

Chemical composition of the powders used in research

	%Al	%Ni	%Fe	%Co	%Cu	Others
Aluminum powder	99.2	-	0.15	-	-	0.15%O_2 0.50%N_2
Nickel powder	-	99.9	0.006	0.07	0.003	($S+C+O_2$) 0.021

In order to obtain the Al-Ni powder mixtures designed for mechanical alloying, have been used aluminum powders with an average diameter of 12.5μm or nickel powders with an average diameter of 90 μm, ($\overline{D_{Al}} = 0{,}14\overline{D_{Ni}}$) dispensed in equal proportions.

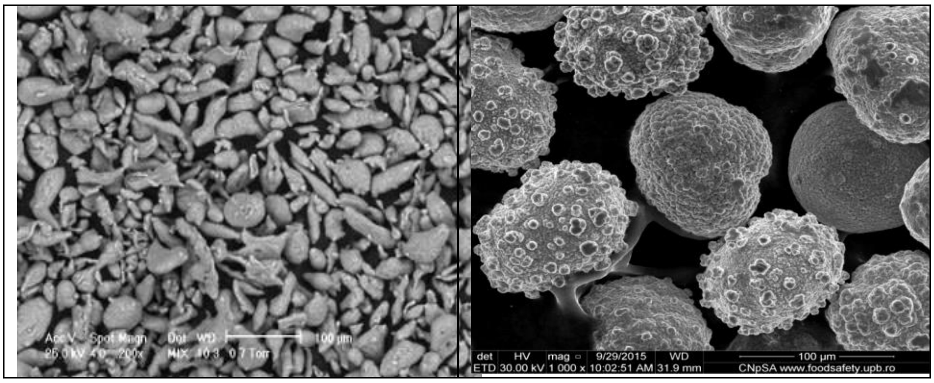

Fig. 1 - Morphology of powders used in the research: aluminum powder (left) obtained by air spraying (Alcoa process) by Zlatna - Romania and nickel powder (right) obtained by Scherritt hydrometallurgical process by Alfa Aesar –Germany.

The synthesis of nickel aluminides by mechanical alloying was performed in ball mills. To measure the grinding bodies released energy during mechanical alloying and to emphasis the difference induced by the grinding bodies weight we used two ball mills one fully ceramic and the other made of refractory steel with sintered hard-alloy grinding bodies (Widia type). The similarities in the operation of the two mills are related to the speed ~ 102 revolution/ min – a value representing 85% of their critical speed (~120 revolution/ min); the differences are related to the weight of the grinding bodies, namely the use volume of the mills: 4,5 kg in the case of metal mill provided with sintered metal carbide grinding bodies (23 balls with the diameter of 30 mm), at a volume of 2.5 liters respectively 0.3 kg in the case of the ceramic mill (17 ceramic balls with the diameters between 18 and 34 mm) at a volume of 1.5 liters the results, obtained in different processing conditions, corresponding to the mechanical alloying in ball mills, were investigated by electronic scanning microscopy (microscope TESCAN VEGA XMU 8) and X-ray diffraction (diffractometers APD 2000 and X'pert PRO MPD PANalytical).

3. Experimental results and discussions;

The energy released by the grinding bodies (Et), when the mill is in use, represents a sum of the kinetic energies (Ec) released by the grinding bodies during their rolling on the slope created by themselves (cascade movement) and potential energy (Ep) released by them as a result of free fall from near the zenith point of the mill. In the specialty literature, there are many tests meant to estimate the energy of grinding bodies, when the ball mills are used [14; 15; 16] and they are generally performed simultaneously with the tests for the calibration of mills' drive engine power [16; 17; 18]. The estimation of Pritâkin E. D. [15] related to the kinetic energy of the grinding bodies starts from the weight of the load (m), from the distance of the load's inertia center in relation to the geometric center of the mill (R_0) and from the angle α representing the tilt angle of the load's weight center at which the load detaches from the wall of the mill (initiation of the cascade operating mode) [ec. 3].

$$E_c = \frac{m}{2} g R_0 \cos\alpha \qquad [15] \tag{3}$$

For a value of the angle α=54°45’ [14], cosα = 0.577 (at a degree of loading φ = 0.4) [15], it results a value of the kinetic energy:

- E_c ~ 0.689J, in the case of metal mill provided with grinding bodies made of sintered metal carbides (for the load weight of 4.5kg + 0.040 kg = 4.54kg, and a ratio between the weight of the grinding bodies and the weight of the load ~ 110), respectively
- E_{c1} ~ 0.06J, in the case of ceramic mill provided with ceramic grinding bodies where the weight of the grinding bodies is 300g and the weight of the material that must be fragmented is 100g (the ratio of the two sizes is 3);
- E_{c2} = 0.055J, in the case of the ceramic mill provided with ceramic grinding bodies where the weight of the grinding bodies is 300g and the weight of material that must be fragmented is 66.5g (the ratio of the two sizes is ~ 4.5);
- E_{c3} = 0.0505J, in the case of the ceramic mill provided with ceramic grinding bodies where the weight of the grinding bodies is 300g and the weight of material that must be fragmented is 33g (the ratio of the two sizes is 9.09).
- The possible energy (Ep) of grinding bodies is added to this value

$$E_p = mgY \tag{4}$$

where *Y* represents the height to which the grinding bodies are lifted; it is equal to the sum of the inner/ working radius of the mill (R) and the distance from the center of the mill to the free surface of the load (R_1), Y = R + R_1). There is a correlation between the sizes R_o-R and R_1 (ec. 5 from ref. [15]):

$$R_0 = \sqrt{\frac{\left(R^2 + R_1^2\right)}{2}} \tag{5}$$

so that, for R=0.062m and R_o=0.0537m, in the case of the mill provided with grinding bodies made of sintered metal carbides, it results the following values:

R_1 = 0.0438m and respectively, Y ~ 0.106m.
Ro, R, R1 and Y sizes are common to both mills.

Ep = (4.5+0.04) ×9.81×0.106 = 4.716 (grinding bodies made of carbides)

It results that the energy (released by the grinding bodies made of sintered metal carbides) for a full revolution of the load is E_t=E_c+E_p=0.689+4.716=5.405J. As it is when the body of the mill performs one full revolution, the load performs a plurality of cycles (n), so that the total value of the energy released will be higher *(E'= n×Et)*

According to the methodology of Andreev [19]:

$$n = \left(1 - k^2\right) / \varphi \tag{6}$$

Where $k = R_1 / R = 0.0438 / 0.062 = 0.706$

and φ = 0.4 represents the degree of the mill's load it results:

$$n = \left(1 - 0.706^2\right) / 0.4 = 1.25$$

Consequently, in the case of the mill provided with grinding bodies made of metal carbides, the total energy released by the grinding bodies at a full revolution of the mill's body will be: E'= n×Et = 1.25×5.405 = **6.75J**

Similarly, in case of the ceramic mills, the possible energy of the grinding bodies will be**:**

E_{p1} = (0.3+0.1) ×9.81×0.106 = 0.415J; for 100g processed material

E_{p2}= (0.3+0.0665) ×9.81×0.106 = 0.380J for 66.5g processed material

Ep3= (0.3+0.033) ×9.81×0.106 = 0.346J for 33g processed material

When added to the kinetic energies corresponding to the weights of the material processed, the values lead to a total level of energy is E_{t1} = 0.06 + 0.415 = 0.475J; E_{t2} = 0.435J; E_{t3} = 0.396J.

Further to the correction, results **E_{t1}'=0.593J; E_{t2}'=0.544J; E_{t3}'=0.495J**; the energies released by ceramic grinding bodies at a full revolution of the mill' body and different weights of the material processed (ratio of the grinding bodies' weight and the weight of the material processed within falls the limits of 3 ÷ 9). When comparing the calculated value of the energy released by the grinding bodies with the minimum value required for the beginning of fragmentation of the powder particles [20] in the mixture undergoing the mechanical alloying (E_0, [10] - (eq.7), it is noticed that the conditions for further particles fragmentation are created during the mechanical alloying in the balls mills:

$$E_0 = 8\frac{q}{C}\left[R^2\left(\frac{n}{30}\right)^2 - 2R^4\left(\frac{n}{30}\right)^6 + R^6\left(\frac{n}{30}\right)^{10}\right] = 0.66J \text{ in case of the mill} \tag{7}$$

provided with sintered metal carbides grinding bodies, respectively 0.044 J in the case of the mill provided with ceramic grinding bodies.

In relation 7 the meaning of the physical sizes is: *q* the weight of grinding bodies [Kg], *C* the constant that depends of the grinding environment (C = 0.57, in the case of mechanical alloying performed in a dry environment); *R*– the radium of the mill's body [m], *n* mill's speed [rev./ min]. If considering the real speed of the mills used in the research (102 rev./ min), it results that the speed at which the energy is released by the sintered metal carbides grinding bodies, respectively the one consumed during the formation of the nickel aluminides by mechanical alloying is 11.47J/s (11.47 W) and, respectively, in the case of the mills provided with ceramic bodies 1 J/s (1W) for 5 hours of operation; 0.92J/s (0.92W) for 10 hours of operation and 0.84 J/s (0.84W) for 15 hours of operation. Over the time, the energy (released by the grinding bodies, respectively the energy consumed during the mechanical alloying process) reaches the values of 9.2 Wh; in case of ceramic mills after 10 hours of operation and, respectively, 573.5Wh in the case of the mills provided with grinding bodies made of sintered metal carbides, after 50 hours of operation. The experiments conducted in the low-energy mill for 5, 10 and 15 hours led to the conclusion that the kinetics of the nickel aluminides synthesis is slow, their ratio being below 6% for the maximum processing time (Fig. 2). Ratio of the nickel aluminides reaches the maximum after 10 hours, and then remains quite constant).

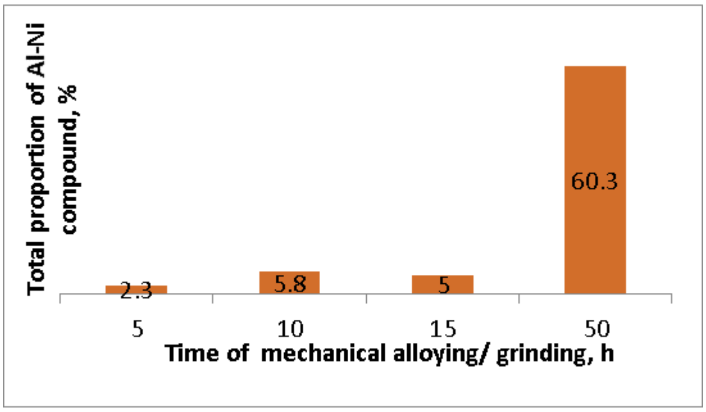

Fig. 2 Variation of the ratio of the nickel aluminides in the powder mixture Al-Ni (1:1), mechanical alloyed in various-energy ball mills: in the case of ceramic mill 1 J/s for 5 hours of operation, 0.92 J/s, 10 hours of operation and 0.84 J/s for 15 hours of operation, respectively 11.47 J/s for 50 hours of operation of the sintered metal carbides ball mill.

In the case of mechanical alloying in low-energy mills (ceramic mills), the detected peaks for nickel aluminides were of the Al_3Ni_5 type (Figs. 3 to 5). By using high-energy mills (mills provided with sintered metal carbide bodies) for long periods of time (50 hours), the effects of the mechanical alloying are much more obvious, both by the total proportion of the resulted intermetallic compounds, 60.3% of the initial aluminum and nickel powders, and by their diversity (Fig. 6): 35.6% Al_3Ni_2; 15.8% Al_3Ni_5; 8.9% $AlNi_3$. Since the mechanical alloying induces a high proportion of defects in the powder particles undergoing the processing, the solubility limits of the reactants change substantially. Thus, in equilibrium conditions the solubility of nickel in the aluminum solid phase is zero and during the mechanical alloying process it becomes significant, reaching up to 10% and the nickel reduces its capacity to solubilize the aluminum up to 0.5% [4]. The two elements (aluminum and nickel) can be one in relation to the other one, solvent and solution, the ambivalence of their behavior being dictated by their mutual solubility. Under these circumstances, it is obvious to find in the mechanically alloyed Al-Ni powder mixture samples the full range of system-related phases, in proportions that depend on the conditions in which the process was conducted (on the energy released). The formation of both equilibrium and metastable solid solutions during the mechanical alloying can therefore be attributed to the effect of plastic deformation. The role of plastic deformation is to refine the particles and crystal grains size (therefore, to increase the total area of the grain limits), as the decrease of the particle's size causes the decrease of the distance along which the transfer of weight between the particles occurs by diffusion, thus favoring the diffusion by the pipe diffusion (through dislocation channels, according to the model proposed by Estrin [21]). The intensity of the weight transfer phenomena, on limits and in volume, is also favored by the increase of the defects' density and of the local temperature (the effect of the impact energy transformation in thermal energy).

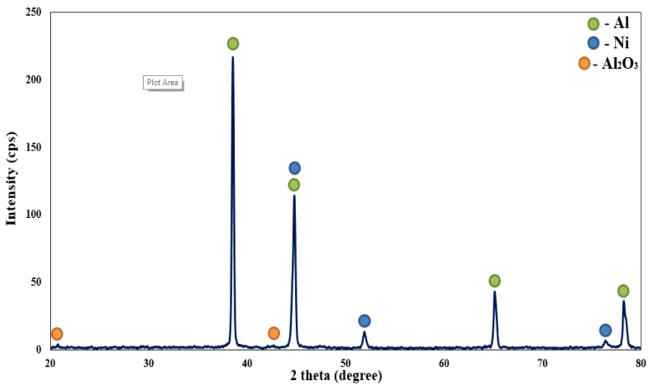

Fig. 3. Diffractogram of the nickel's Al-Ni-aluminides powder mixture resulted after after 5h of mechanical alloying, of the Al-Ni mixture (1:1) in low-energy ceramic mills (Et = 0.593 J/rev. and 5Wh is the energy released by grinding bodies during those 5h

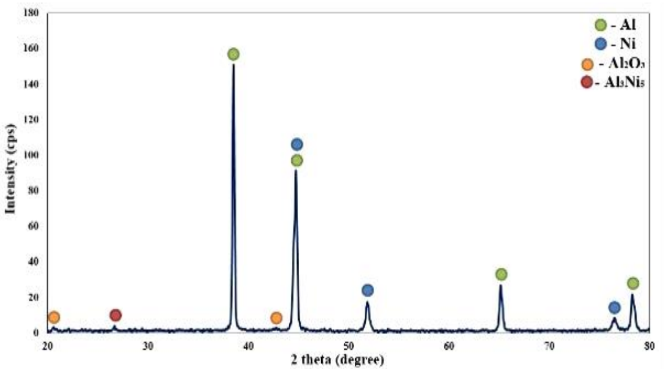

Fig. 4. Diffractogram of the nickel's Al-Ni-aluminides powder mixture resulted by 10-h. of mechanical alloying, of the Al-Ni mixture (1:1) in low-energy ceramic mills (Et = 0.544 J/rev. and 9.2 Wh is the energy released by grinding bodies during those 10 h.

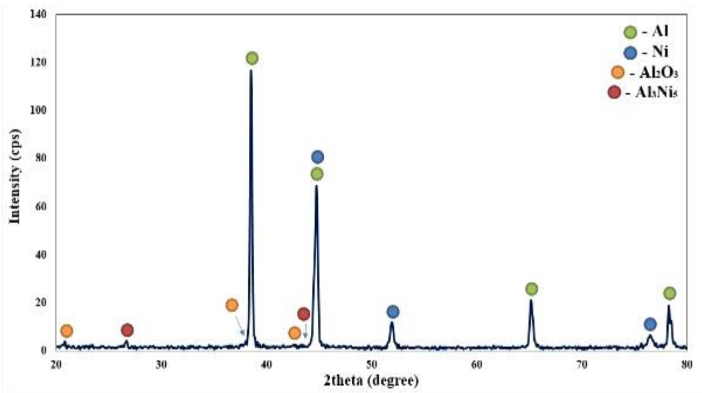

Fig. 5. Diffractogram of the nickel's Al-Ni-aluminides powder mixture resulted by 15-h. of mechanical alloying, of the Al-Ni mixture (1:1) in low-energy ceramic mills (Et = 0.495 J/rev.and 12.6 Wh is the energy released by grinding bodies during those 15 h.

The comparative analysis of diffractograms from Figs. 3 to 5 highlights the fact that the intensity of the diffraction lines corresponding to the pure metals (aluminum and nickel) decreases to time, along with the emergence and development of the proportion of intermetallic compounds (nickel aluminides). The diminished value of the ceramic mills' energy at which the weight of the grinding bodies was maximum 300g, dictated an impact energy within the limits of 0.5 up to 0,6 J/ revolution (depending on the actual amount of loads 'weight) and did not allow a substantial conversion of the two reactants (the aluminum and the nickel) in their specific compounds, so that an increase of the processing time within the limits of 10 ÷ 3 hours ensured a conversion of 5 ÷ 6%. The intensity of the phenomena specific to the mechanical alloying increases, on the one hand, due to the change of the grinding bodies' weight (from 0.3kg to 4.5kg) and, on the other hand, due to the increase of the ratio between their weight and the weight of the powder undergoing processing; thus, in the case of ceramic mill, the value of this ratio varied within the limits of 3 ÷ 9 (it increased in the same time the processing time increased, by the extraction at every 5 hours of equal amounts of powder out of the mill) by contrast to the mill provided with sintered metal carbide grinding bodies, where the value of this ratio remained constant in time: 110 (for a processing time of 50 hours). In these conditions, the rate of conversion of the elemental Al and Ni powders into the intermetallic compounds specific to them exceeds the level of 60% (Fig. 6) while increasing at the same time the diversity of the aluminide type, from those rich in aluminum (Al_3Ni) to those rich in nickel ($AlNi_3$).

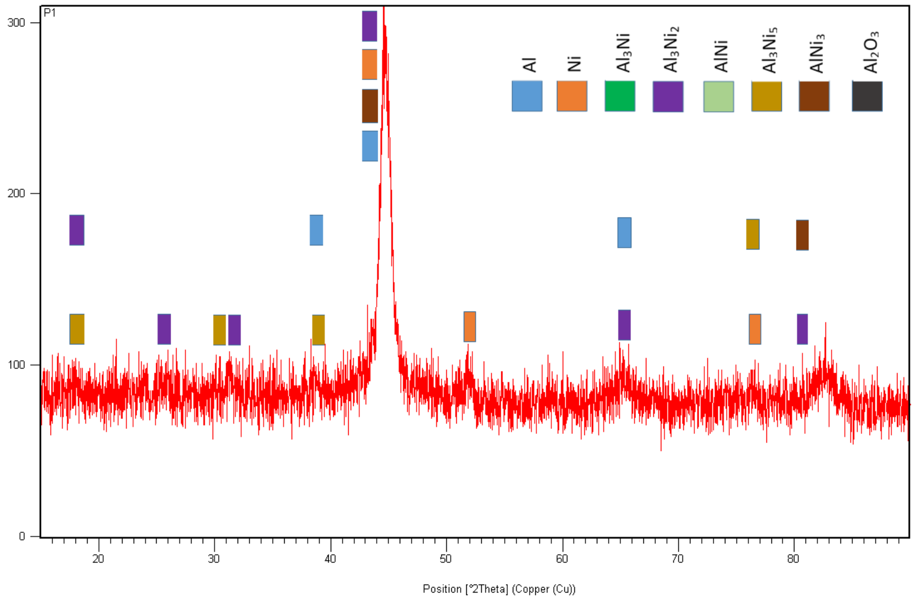

Fig.6. Diffractogram of the nickel's Al-Ni-aluminides powder mixture resulted by 50-h. of mechanical alloying, in the mill provided with sintered metal carbide grinding bodies (Et = 6.75 J/rev. and 573.5Wh is the energy released by grinding bodies during those 50 h.

The differences between the amounts of energy released by the grinding bodies upon the impact with the powder that undergoes fragmentation and the processing time determine an obvious change of the powder's size grading (Fig. 7); a finer and dimensionally more uniform powder in case of mechanical alloying in high-energy mills.

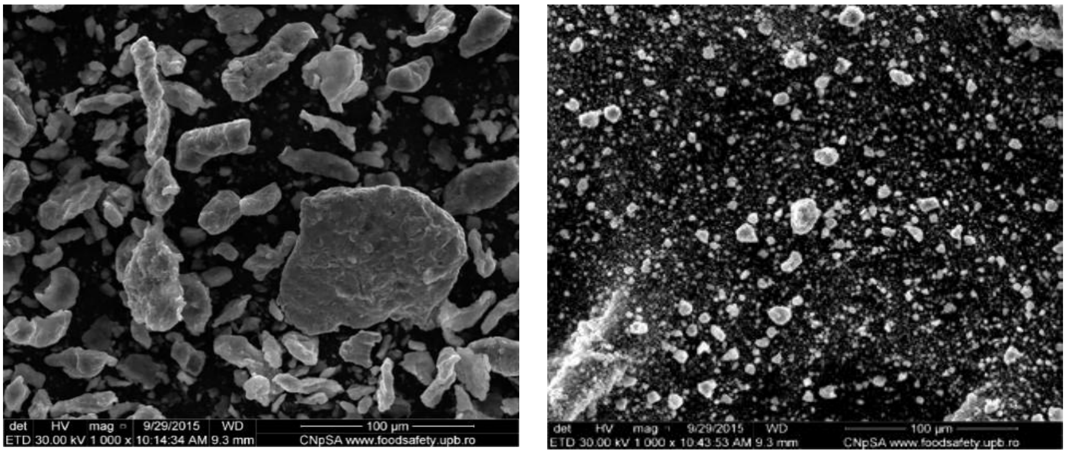

Fig. 7. Morphology of the powder particles obtained by mechanical in: *(a)low-energy ball mills for 10h; (b) high-energy ball mills for 50h.*

The morphology of the powder particles resulted from mechanical alloying (Fig. 8) is similar, since it reflects the complex mechanisms underlying the mechanical alloying: deformation of particles, mutual welding, fragmentations, redeformations, reweldings, refragmentations, etc. Obviously, the occurrence of hardening and recrystallization phenomena is very probable.

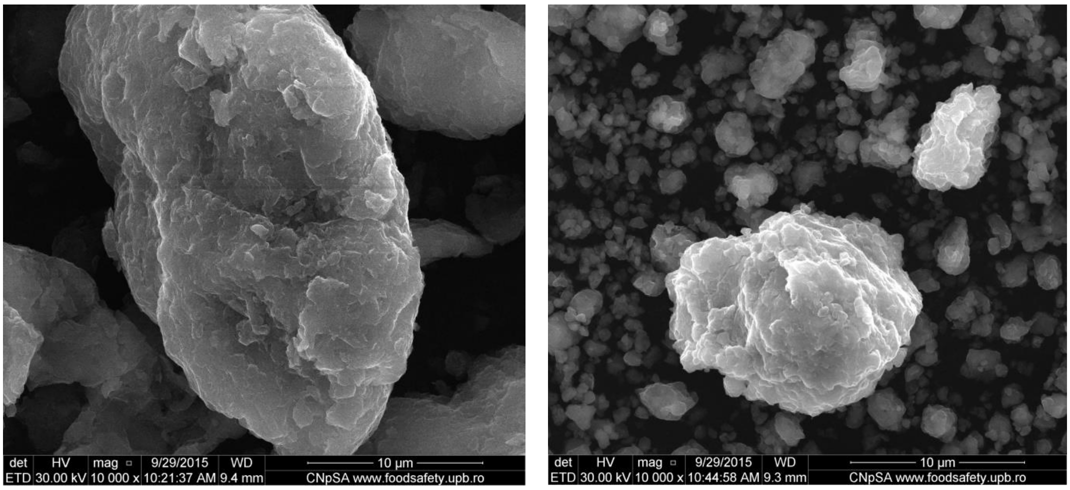

Fig. 8. Morphology of the powder particles obtained by mechanical alloying in : *(a) low-energy ball mills, 0.495J/rev, 15h; (b) high-energy ball mills, 6.75J/rev., 50h. SEM images*

4. Conclusions

The experimental researches in the field of nickel aluminides synthesis by means of mechanical alloying in ball mills, revealed the following aspects:

- The ball mills specific energy (the one released by the grinding bodies at a revolution of the mill's body) is directly proportional with the load's weight and with the geometric feature of the mill, expressed by the distance between the geometric center of the mill and the distance between the weight center of the load (R_0. This statement is valid for a value of tilt angle of the load's weight center
- α_o =54°45', when it detaches from the mill's wall. There was estimated the specific energy of the two mills with the weight of the grinding bodies of 0.3kg, respectively, 4.5kg and the amount of energies released/consumed during the process of mechanical alloying performed on specified time intervals;
- In the case of light-weight loads, the impact specific energy is lowered, so that the increase of the mill's running time and of the ratio between the weight of the grinding bodies and the weight of the material undergoing fragmentation would not cause an essential change to the proportion of the synthesis products resulted from the interaction of the components; in the case of high-energy mills the conversion rate of the interacting metals is substantially increased; the same happens with the diversity of the type of compounds, resulting from mechanical alloying;
- Mechanical alloying can create energy conditions required for further fragmentation occurring during the nickel aluminides synthesis process.

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