THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
Nº. 1 - 2020, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2020.1.03

REINFORCED Al-MATRIX COMPOSITES WITH Ni-ALUMINIDES, PROCESSED BY POWDERS

Mihai Ovidiu COJOCARU[1,2], Mihai BRANZEI[1*], Florica TUDOSE[1], Leontin Nicolae DRUGA[2]
[1]University POLITEHNICA of Bucharest, Bucharest, Romania
[2]Technical Sciences Academy of Romania, Bucharest, Romania
e-mail: mihai.branzei@upb.ro

ABSTRACT

The paper addresses issues of interest related to the uniform distribution of the reinforcement phase and the continuity of the metal matrix, for two ways of obtaining the powder composites, the hot extrusion and the spark plasma sintering (SPS) respectively. The reinforcement phase is the nickel aluminides obtained by mechanical alloying in ball mills, and the metal matrix is made of aluminum powders. Prior to extrusion, the mixture of aluminum powders and nickel aluminides was pressed and subsequently sintered in environments with high carbon potential, so that in the final product, nickel aluminides, carbide and aluminum oxides were found as reinforcement phases. The obtained results confirmed the hypothesis that, from a blank product with a random distribution of the reinforcement phase, a product with an ordered distribution of the reinforcement phase is obtained after extrusion and that for the same initial proportion of nickel aluminides as reinforcement phase, the composite hardness obtained by hot extrusion is higher compared to that obtained by SPS, the difference being determined by the increase of the proportion of the reinforcement phase by the appearance of aluminum carbide and aluminum oxides during the sintering operation in the high carbon environment.

KEYWORDS: Ni-aluminides, mechanical alloying, hot extrusion, Spark Plasma Sintering (SPS), coated composite particles

1. Introduction

Aluminum and its alloys represent an important class of materials due to their versatile properties. This aspect allows its use in a wide range of applications, many of them having it as a matrix in which hard phases are included, with high thermodynamic stability. The refractory intermetallic compounds in the Al-Ni system are of particular interest due to their intrinsic characteristics, their presence increasing the operating characteristics of the matrices that contain them. In the presence of nickel aluminides dispersed in the aluminum matrix, there is a substantial increase in wear resistance, hardness, oxidation resistance, improvement of carburizing and nitriding processes, as well as thermodynamic stability. Nickel aluminides represent phases with high potential for increasing the performance of metal or light alloys. Of the five aluminides present in the Al-Ni system (Al_3Ni_2, Al_3Ni_5, Al_3Ni, $AlNi_3$, AlNi) [1, 2], the last two are characterized by extremely high thermodynamic stability at temperatures above 1000 ºC, associated with ductility, hardness, high mechanical resistance associated with oxidation resistance, carburizing and nitriding [3].

The conclusions of a large experimental research conducted by Gessinger [3], led to the idea that obtaining composites containing intermetallic compounds (IMCs) such as nickel aluminides, through the traditional steps of powder metallurgy (pressing at ambient temperature followed by sintering), does not lead to satisfactory results, for two main reasons: i) the magnitude of the elastic recovery phenomenon after pressing, determined by the nickel aluminides hardness and thus their reduced plasticity; ii) the substantial decrease of the capillary forces in the presence of mechanically allied powders particles of large dimensions (60-100 μm) and with high hardness, phenomenon that determines the substantial shrinkage reduction during sintering [3].

Consequently, the conventional technologies for the manufacture of such composites should combine the two pressing and sintering steps into one, so that by changing the character of the aluminide from fragile to ductile, it becomes possible to ensure the desired densification and imposed physical and implicit structural features [3, 4].

The main methods of processing composites containing reinforcement phases such as nickel aluminides are hot isostatic pressing, electric current activated/assisted sintering (ECAS), widely known as spark plasma sintering (SPS) and hot pressing (hot extrusion process derived from it) [5].

2. Materials and experimental methods

The aluminium and nickel powders used in this research were obtained by air spraying (aluminium powder, purity ~92 %, manufactured by Zlatna, Romania), or by Sherritt Hydrometallurgical process (purity 99.9% manufactured by Alfa Aesar part of Thermo Fisher Scientific, Germany). In order to obtain the Al-Ni powder mixtures designed for mechanical alloying, have been used aluminium powder with an average diameter of 12.5 µm and nickel powder with an average diameter of 90 µm, dispersed in equal proportion.

The mechanical alloying was made in ball mills (2.5 l volume capacity), at 85% of the critical speed value (~102 rot/min), so that the released energy would be 8 J/rot (about 13 J/s), at one about 11:1 ratio between the mass of the milling balls and that of the powder mixture, consisting of equal mass proportions of aluminium and nickel powders.

The calculation of the total energy released by the milling bodies took into account the mill geometrical and functional characteristics, the milling bodies and the powder mixture masses subjected to processing, and so on [6-12].

The experimental research steps are presented in the form of a scheme, as shown in Figure 1.

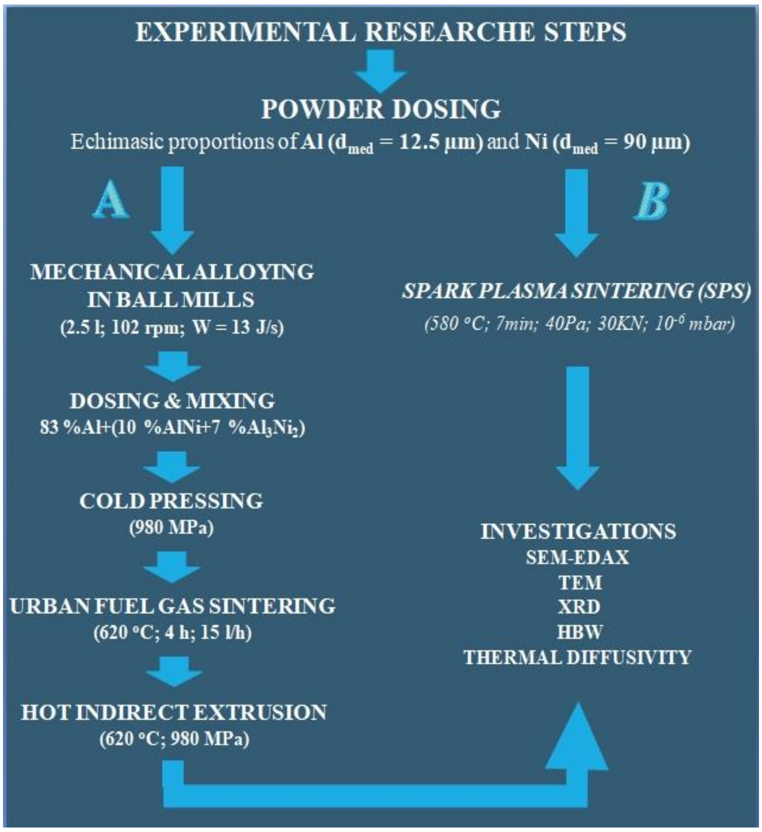


Fig. 1. *Experimental research steps*

Cold pressing was performed hydraulically (60 tf), with uniaxial and unilateral effort application; the same press was used for extrusion, the extrusion die being heated to 650 °C. Heating for sintering was carried out in a furnace provided with automatic temperature control (UTTIS Industries-Romania), at a temperature value below that of melting the aluminum matrix (620 °C), maintenance for 4 hours,

Nº. 1 - 2020, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2020.1.03

in an environment resulting from the thermocatalytic dissociation of urban fuel gas, which contains about 85% methane, at a flow rate of 15 l/h.

SPS was performed on a spark plasma sintering furnace for field assisted sintering technique (FAST), from FCT Systeme GmbH, HPD5 type facility, from Germany.

The results obtained under the different processing conditions, were investigated aiming to highlight the microstructural changes involved and the physical and mechanical properties.

Scanning electron microscopy (SEM -TESCAN VEGA XMU 8 microscope), EDS (EDAX Sapphire type dispersive energy spectrometer with the resolution of 128 kV), X-ray diffraction (APD 2000 diffractometer), transmission electron microscopy (TEM - JEM ARM microscope 200F; the samples were prepared by mechanical thinning, followed by precision ion polishing at small incidence angles, in argon atmosphere, with the aid of a GATAN PIPS System Model 691), appliance were used.

In order to highlight the physical and mechanical characteristics changes, a Heckert hardness tester, series 308/278, was used. For the tests performed, the device was equipped with a tungsten monocarbon ball of 2.5 mm in diameter, applying at a 612.9 N load. Hardness measurements (HBWm) were performed according to the DIN EN ISO 6506, and the data has been processed according to the "Arghir" methodology [13, 14]:

$$HBW_m = 1/6n\left(n \times HBW_0 + 3n \times HBW + 2n \times HBW\right) \quad (1)$$

where:

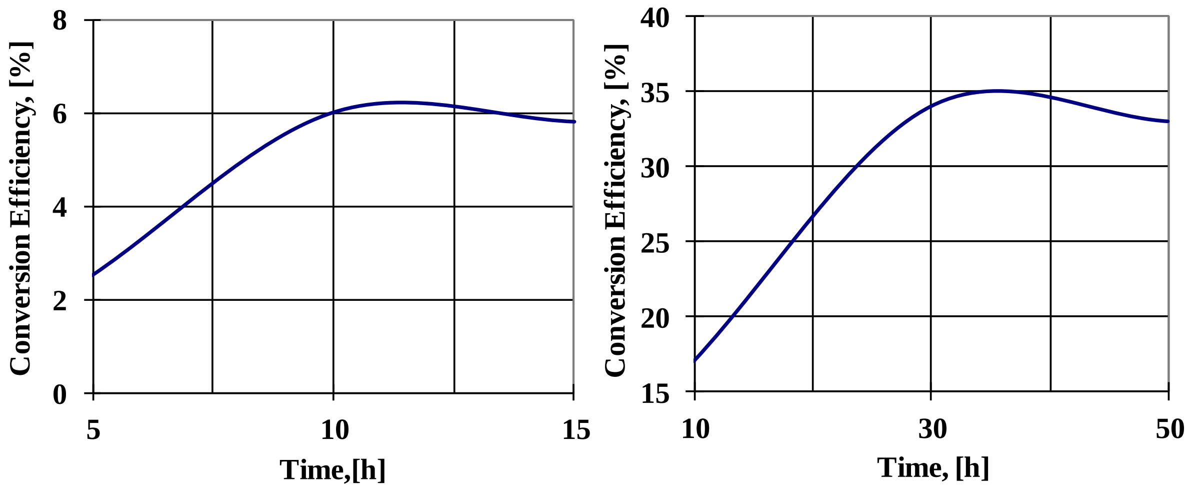
- HBWm is the average value of macrohardness;
- HBWo represents the hardness measured in the center of the sample;
- HBW is the value of the macrohardness at half sample radius.

Thermal diffusivity (α) tests were performed on a Netzsch apparatus, model LFA-457, at 20 ºC. The principle of design, construction and operation of the apparatus is based on the flash method.

The results of the diffusivity measurements are the average of six tests.

3. Results and discussions

The elemental aluminum and nickel powders conversion into intermetallic compounds (IMCs), during mechanical alloying in ball mills, depends directly on the energy released by the milling balls (W) and the grinding time, as it is shown in Figure 2.
Thus, the increase of the energy released by the milling balls has the first effect of increasing the conversion efficiency (compare Figure 2a with 2b), and as it increases, the ratio between the Ni-rich and the Al-rich aluminides respectively changes [8].



Note - To highlight the effect of the energy low values (<1 J/rot - Figure 2a) on the conversion efficiency, a ceramic mill with a useful volume of 1.5 l was used, the ratio of the balls mass to the load mass was 3:1

***Fig. 2.** Conversion efficiency variation according to the energy released by the milling balls and the processing time: a) energy of 0.7 J/rot at 102 rpm; b) energy of 7 J/rot at 102 rpm*

In the present case, for the energy values of the milling balls below 1 J/rot, the mechanical alloying will lead to Ni-rich aluminides (Al_3Ni_5) higher values obtaining. At higher values, Al-rich aluminides

THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N°. 1 - 2020, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2020.1.03

(AlNi, Al_4Ni_3, Al_3Ni_2) will be the majority. In time, the production rate of the elemental powders mixture conversion into intermetallic compounds decreases, so that the prolongation of the milling under certain energetic conditions becomes inefficient.

Starting from these conclusions, obtaining nickel aluminides by mechanical alloying in ball mills was performed under the conditions: W = 7 J/rot; n = 85 % ncr = 102 rpm; t = 30 hours. Under these conditions, starting from an equal weight mixture of elemental aluminium and nickel powders, a new powders mixture containing 34 % nickel aluminides (20 %AlNi and 14 %Al_3Ni_2) resulted. This new mixture was used as the reinforcing phase of the powdered aluminum matrix.

The blank product for hot extrusion was done by pressing (980 MPa). Sintering was carried out in the urban fuel gas atmosphere from the industrial network (about 85 %CH_4), at the following parameters: 620 °C, 4 hours; 15 l/h urban fuel gas). The powder mixture was made up of 50% aluminium powder and 50% mechanically allied powder containing about 17% nickel aluminides (AlNi + Al_3Ni_2).

The formed sinter/composite microstructure (Figure 3) is characterized by a relatively uneven distribution of the reinforcement phase in the metal matrix.

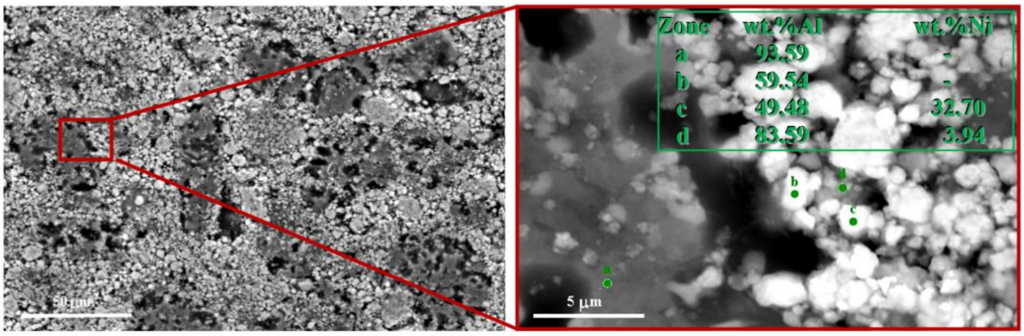
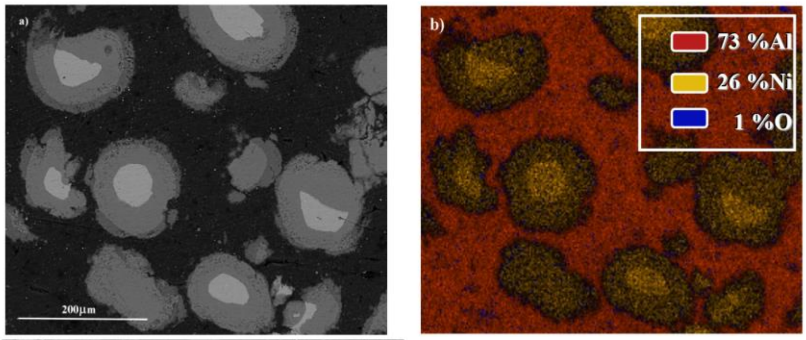
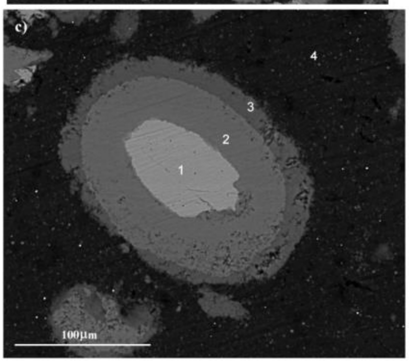


Fig. 3. *SEM-EDS images of the aluminium matrix hardened with 17 % nickel aluminides (10 %AlNi and 7 %Al_3Ni_2), with elemental composition details in different interest microvolumes*





	wt. %Al	wt. %Ni
Zone **1**	78.62	15.90
Zone **2**	44.13	53.91
Zone **3**	63.01	32.69
Zone **4**	90.24	1.30

Fig. 4. *SEM images of the sintered and hot extruded material: a) image of secondary electrons; b) EDS image for elemental distribution; c) the cross-section composite particle with the Al and Ni elemental distribution, by EDS spectrometry table*

N°. 1 - 2020, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2020.1.03

Its average macrohardness has values of 58 HBW, the thermal diffusivity at ambient temperature being 4.85 mm^2/s (5 % of the value related to the technical purity aluminium), and the thermal conductivity being 29.7 W/mK (12.5 % of the value related to the technical purity aluminium).

By hot extrusion of the pressed and sintered composite (Figure 4), an ordering of the reinforcement phase in the flow direction is obtained (Figure 4b) and a significant increase of the macrodurity of 2.77 times higher than that of the sintered composite.

To this high value of the macrohardness, besides the nickel and oxide aluminides and respectively the aluminum carbide, during the sintering in urban fuel environment formed.

X-ray diffraction pattern (Figure 5) confirms the presence of aluminum carbides and oxides.

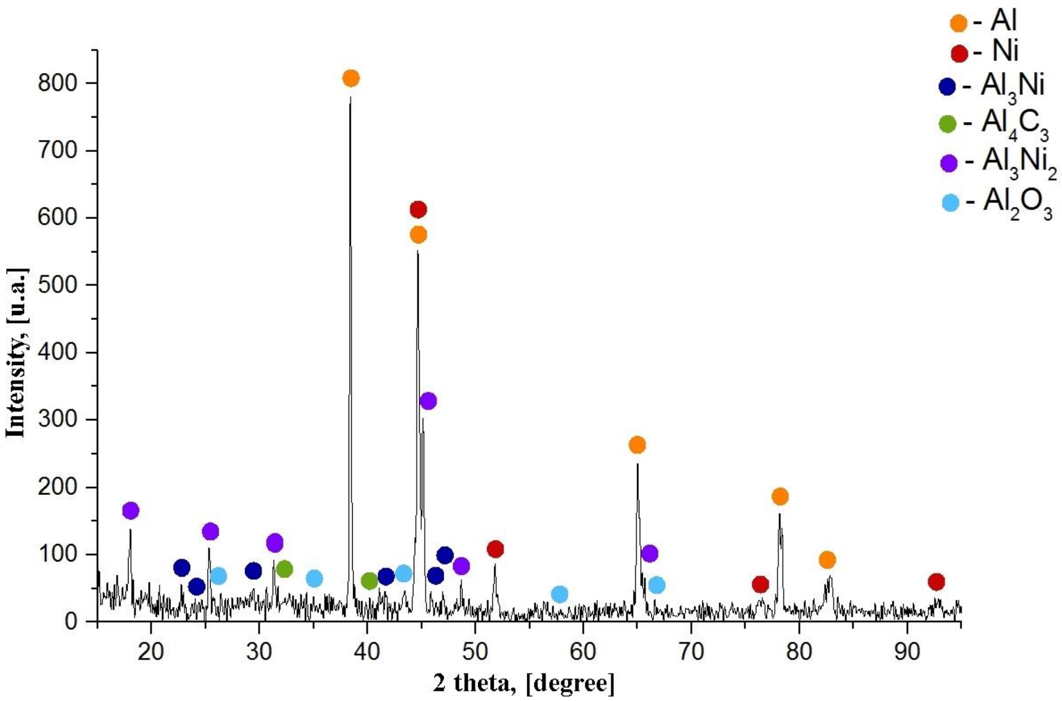


Fig. 5. *X-ray pattern of the extrudate with 17 % nickel aluminides (10 %AlNi and 7 %Al_3Ni_2) and aluminium balance*

The aluminium carbide and aluminium formation and growth respectively is extremely likely from a thermodynamic point of view, as it shown in the reaction (2-4) [15]:

$$4Al + 3C = Al_4C_3 \qquad (\Delta G = -127.7 \;\; kJ/mol \qquad \Delta H = -219.4 \;\; kJ/mol) \tag{2}$$

$$4Al + 3CH_4 = Al_4C_3 + 6H_2 \qquad (\Delta G = -200.8 \;\; kJ/mol \qquad \Delta H = +48.8 \;\; kJ/mol) \tag{3}$$

$$4Al + 3O_2 = 2Al_2O_3 \qquad (\Delta G = -2791.3 \;\; kJ/mol \qquad \Delta H = -3345.9 \;\; kJ/mol) \tag{4}$$

The carbon required for aluminum carbide synthesis can come from both the magnesium stearate ($C_{36}H_{70}MgO_4$) decomposition, a lubricant used for mixtures homogenizing and obviously for extrusion, as well as from the methane used as a sintering medium (CH_4 thermocatalytic decomposition products).

The aluminum oxide is formed during sintering and is preferentially distributed within the boundary area, as it is shown in Figure 4 b,c).

High resolution TEM investigations revealed the presence of oxide films at the matrix interface with the aluminum powder particles, respectively aluminides boundary, as it is shown in Figure 6.

THE ANNALS OF “DUNAREA DE JOS” UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N°. 1 - 2020, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2020.1.03

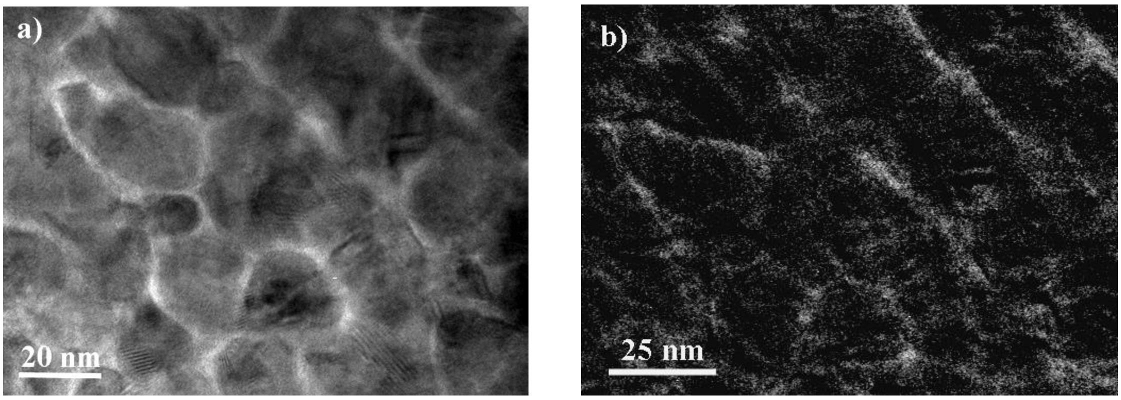


Fig. 6. *High resolution TEM images of the aluminum matrix hardened with nickel aluminides: a) high resolution image; b) Oxygen mapping*

The particularities of the indirect hot extrusion operation, carried out after sintering, according to the triaxial stress scheme (S1), ensure the possibility of producing blank products without discontinuities [16].

The reinforcement phase (including the oxides initially disposed predominantly at the boundaries) is thus uniformly distributed and preferably oriented in the deforming direction.

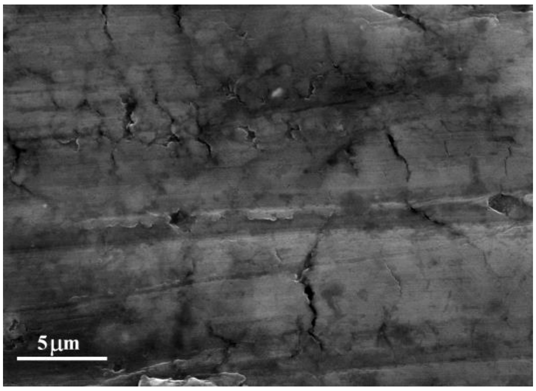


Fig. 7. *SEM image of the composite material after the final hot pressing at 350-400 °C, 980 MPa*

If the extrusion after the sintering is replaced by a hot plastic deformation, at 350-400 ºC (also using the heat stored on the sintering), the spatial stress scheme modification from S1 (triaxial compression) to S3 (compression and two extensions), definitely generates discontinuities in blank, also verified by experiment, the SEM image in Figure 7 being representative.

The SPS ensures the possibility of substantially shortening the general technological cycle of composite materials, resulting in a relatively uniform distribution of the aluminides in the aluminum matrix (see Figure 8).

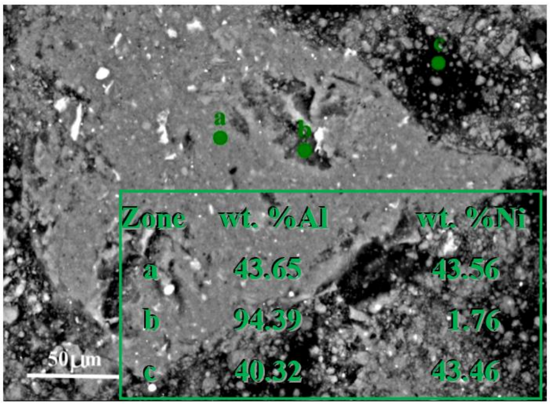


Fig. 8. *SEM image of the composite material obtained by SPS in the processing conditions 580 °C, 7 min, 40 Pa, 30 kN and the elemental analysis table by EDS spectrometry in the areas of interest*

Macrohardness will increase by about 80% compared to that of composites made by cold pressing and sintering (100 HBW versus 56 HBW), the thermal diffusivity will be reduced by half compared to that of sintered aluminum (41 mm^2/s compared to 82 mm^2/s).

4. Conclusions

Mechanical alloying in ball mills, at over 8 J/rot value of the energy released by the milling balls, can provide in about 30 hours the conversion yields of the elemental aluminum and nickel powder mixtures in Al-rich nickel aluminides, on the order of 30 percent.

The hot extrusion applied to the semi-finished products made of mixed nickel aluminum/aluminide powders pressed and subsequently sintered in atmospheres with high carbon potential, ensures a high density of the composite and a continuity thereof. At the same time there is an ordering of the reinforcement phase in the material deformation direction during extrusion.

Under the special conditions of hot extrusion, it is possible to form composite particles with a morphology analogous to the of the coated one.

The average macrohardness of the aluminum matrix composites reinforced with nickel aluminides is about 58 HBW, which is also justified by the presence of carbide and aluminum oxides respectively, phases formed due to the high carbon environment potential, in the presence of oxygen.

The extruded matrix continuity, aluminides, carbides and aluminium oxides hardened, is ensured by the S1 space state tensions, which is characteristic of the extrusion process.

The composites production by SPS allows a considerable shortening of the general manufacture technological flow, a satisfactory matrix continuity level, a reinforcement phase distribution depending on the previous homogenization degree, as well as mechanical characteristics superior to those recorded on the products processed by cold pressing, followed by sintering.

References

[1]. Massalski T. B., Murray J. L., Bennet K. H., Baker H., *Binary Alloys Phase Diagrams*, ASM International, U.S.A., 1986.

[2]. Nash P., Singleton M. F., Murray J. L., *Alloy Phase Diagrams*, vol. 3, ASM International - 2nd Edition, 1992.

[3]. Guard R. W., Yutkalo A. M., *Fractographic Studies in NiAl and Ni_3Al, Mechanical Properties of Intermetallic Compounds*, ed. by Westbrook J. H., John Wiley &Sons Inc., p. 141-160, 1960.

[4]. Yamanoglu R., *Production and Characterization of Al-xNi in Situ Composites using Hot Pressing*, Journal of Mining and Metallurgy, section B: Metallurgy, 50(1)B, p. 45-52, 2014.

[5]. Gessinger G. H., *Powder Metallurgy of Superalloys*, Butterworths and Co, p. 58-103, 1984.

[6]. Yan B., Fang H., Bingyan F., Xing H., *Energy Calculation Model of Ball Kinematics Based on Ball Mill Coal Load*, Journal of Innovative Computing, Information and Control, 10(5), p. 1715-1725, 2014.

[7]. Pritikin B. P., *Mehaniceskoe oborudovanie zavodov ţvetnoi metallurghii*, vol. 1, Mehaniceskoe oborudovanie dlea podgotovki şihtovih materialov, Metallurghia, Moskva, p. 231-232, 1988.

[8]. Bogdanov V. S., Antsiferov S. I., Bogdanov N. E., *The Power Consumption Calculation of a Ball Drum Mill*, Midle Est of Scientific Research, 18(10), p. 1448-1454, 2013.

[9]. Magdalinovic N., *Calculation of Energy Required for Grinding in a Ball Mill*, International Journal of Mineral Processing, 25(1-2), p. 41-46, 1989.

[10]. Andreev A. S., Petrov V. A., Zverevici V. V., *Droblenie, izmelceniei grohocenie poleznih iscopaemih*, Ucebnic dlea vuzov - Nedra M., 1980.

[11]. Thomas A., Filipov L. O., *Fractures, Fractals and Breakage Energy of Mineral Particles*, International Journal of Mineral Processing, 57(4), p. 285-301, 1999.

[12]. Cojocaru M. O., Tudose F., *Synthesis of Nickel Aluminides by Mechanical Alloying in Ball Mills*, UPB Sci. Bull., Series B, 78(4), p. 181-192, 2016.

[13]. Petty E. R., *Hardness Testing*, vol.2, Techniques of Metals Research, Interscience Publisher - John Wiley & Sons, Inc., p. 157-221, 1971.

[14]. Arghir G., *Izmerenie tvëordosti specennîh materialov*, Poroşcovaia metallurghia, nr. 7 (91), p. 101-104, 1970.

[15]. Cojocaru M. O., Druga L. N., Tudose F., *The Effects of Change the Energy Conditions and Synthesis Media Activity on Nickel Aluminides Type and Proportion*, Journal of Engineering Science and Innovation - D. Chemical Engineering, Materials Science and Engineering, Natural Resources, 2(4), p. 59-69, 2017.

[16]. Popescu N., Ghiban N., Ghiban B., Serban N., *Procesarea materialelor metalice prin forjare, matriţare şi extruziune, Procesarea primară a materialelor metalice*, vol. IV, ed. Riposan, I., Tratat de Stiinţa şi Ingineria Materialelor, Ed. AGIR, Bucureşti, p. 1218-1221, 2010.