Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 48
ISSUE 2
October
2011

The influence of initial powder properties on the mechanical alloying process and the final powders structure

W. Pilarczyk*, R. Nowosielski, M. Szymczak
Division of Nanocrystalline and Functional Materials and Sustainable Pro-ecological Technologies, Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland
* Corresponding author: E-mail address: wirginia.pilarczyk@polsl.pl

Received 19.08.2011; published in revised form 01.10.2011

Materials

ABSTRACT

Purpose: The main aim of this work is to study the influence of initial powder properties on the mechanical alloying process and final powders structure and the production of chosen powder alloy by mechanical alloying method.
Design/methodology/approach: The test material was the pure niobium, tin and copper powders. The powders were ground for 2 and 10 hrs. The mechanical alloying process was conducted in a high energy SPEX mill under inert argon atmosphere. The chemical constitution and concentration of particular component were studied by X-ray microanalysis. The changes of the powder structure were tested by means of the X-ray diffractometer. The thermal properties of the chosen powder alloy were examined by DSC method.
Findings: Based on the presented experiment results it is clear that initial powder properties have a large influence on the final powders structure. Most of changes during milling are connected with process parameters and powder properties.
Research limitations/implications: The mechanical alloying technique makes it possible to obtain Nb_3Sn phase but only on a laboratory scale. This is the basic research in the powder metallurgy experiment field. Further investigations should be concentrated on the developing of refinement particles during ball milling, production of the composites and powder consolidation method.
Practical implications: The experiments in this work supply knowledge of ductile and less ductile powders behaviour in mechanical alloying process. This knowledge can be used in powder metallurgy technique.
Originality/value: The obtained investigation result confirm the different course of mechanical alloying process in dependence on powder particles. The synthesis of ductile and brittle powder gives possibility for the development of strengthening new composites by reinforcement particles.
Keywords: Metallic alloys; Mechanical alloying; Powder metallurgy

Reference to this paper should be given in the following way:
W. Pilarczyk, R. Nowosielski, M. Szymczak, The influence of initial powder properties on the mechanical alloying process and the final powders structure, Journal of Achievements in Materials and Manufacturing Engineering 48/2 (2011) 169-176.

1. Introduction

Powder metallurgy can produce metal matrix composites in the whole range of matrix reinforcement compositions [1-4]. One of the main challenges inherent to this technique is to obtain a homogeneous distribution of the reinforcement in the metal matrix [5-10].

To improve particle distribution in the matrix the high-energy ball milling is used. This technique is known as mechanical milling or mechanical alloying [11-13]. Mechanical alloying involves material transfer to obtain a homogeneous alloy by means of repeated deformation, joining and fracture mechanisms. Mechanical alloying is the process in which mixtures of different powders are milled together. Whereas, mechanical milling is the process in which material transfer is not required for homogenization. It consist of powders milling of uniform composition [14-17].

During high-energy ball milling the powder particles are repeatedly flattened, joined and fractured. Whenever steel balls collide, some amount of powder is trapped in between them. The force of the impact plastically deforms the powder particles leading to strengthening and fracture. The new surfaces created enable the particles to join together and this leads to an increase in particle size. If the material combination is ductile-ductile or ductile-brittle, the particles are soft and their tendency to join together and form large particles is high. At this stage the particles are characterized by layered structure. With continued deformation, the particles get hardened and fracture by a fatigue failure mechanism and/or by the fragmentation of fragile flakes [1, 11, 17].

As mentioned above, it is possible to conduct MA of three different combinations of metals and alloys: ductile-ductile, ductile-brittle and brittle-brittle systems. Therefore, it is convenient to discuss the mechanism of MA also under these categories [1, 14, 18-23].

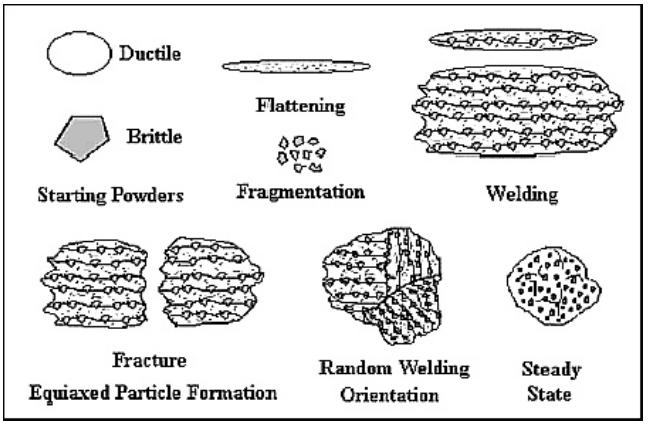

Fig. 1. The various stages of ductile-brittle system during mechanical alloying process [18]

In Fig. 1 Fogagnolo et al. [18] proposed one possible scheme of the mechanical alloying process of ductile-brittle system. At the beginning of process, the ductile particles undergo deformation while brittle particles undergo fragmentation. The brittle particles come between two or more ductile particles at ball collision, whereas ductile particles start to joining. Finally, fragmented reinforcement particles are domicile in the interfacial boundaries of the joined metal particles. The composite particle is formed. As joining is the predominant mechanism in the process, the particles change their morphology by piling up the laminar particles. The authors [18] suppose that these phenomena, deformation, joining and solid dispersion harden the material and increase the fracture process, which contribute to the equiaxed morphology. Then, fracture and joining mechanisms make an equilibrium. At the steady state, the microstructure undergoes a great refinement [1, 11, 18].

2. Experimental procedure

The main aim of this work is to study the influence of initial powder properties on the final powders structure and the producing of Nb-Sn powder alloy by mechanical alloying method.

The metallic powders were chosen and divided for the sake of recrystallization temperature into two groups: ductile powders and less ductile powders (brittle powders).

The division was made on the basis of recrystallization temperature of chosen powders. Copper and tin were used as ductile powders example. Niobium was used as less ductile powder.

2.1. Material

Characteristic of powders used for manufacturing materials is given in Table 1.

Table 1.
Characteristic of initial powder

Chemical element	Copper	Tin	Niobium
Particle size, μm	420	44	44
Purity, %	99.8	99.8	99.8

The atomic and mass concentration of chosen compounds were correlated in Table 2. The weight of particular compounds on 10 grams of sample were calculated.

Table 2.
Atomic and mass concentration of studied metallic compounds

Powder	at., %	mass, %	mass per 10g
Ductile Cu	100	100	10
Less ductile Nb	100	100	10
Less ductile-ductile Nb-Sn	75 Nb 25 Sn	70.13 Nb 29.87 Sn	7.013 Nb 2.987 Sn

2.2. Research methodology

The mechanical alloying process was conducted in a high-energy SPEX 8000 mill of the shaker type under inert atmosphere. The copper powder was mixed for 2, 10, 50 hrs. The niobium powder and Nb-Sn powder alloy were mixed for 2 and 10 hrs. The ball to powder weight ratio was 7.5:1. In this experiment a process control agent was added (1% mass. stearic acid). In order to prevent powder impurities, the samples were sealed in the vial under argon atmosphere.

To identify new phases X-ray examination was performed. The changes of the phase constitution were tested by means of the X-ray diffractometer 7 Seifert-FPM with Co $K\alpha_l$ (l=0.178892), radiation (35 kV, 25 mA). The XRPD data have been collected in steps of 0.04° 2θ and a counting time of 2 seconds per step.

Detailed method description and an evaluation of crystalline size and microstresses were presented in earlier work [19].

The pure, sinter copper was the standard sample in this experiment because it is characterized by perfect diffraction pattern without stresses.

The X-ray microanalysis was carried out by means of the JEOL JCXA 733 scanning electron microscope (SEM).

Using differential scanning calorimetry (DSC) it is possible to observe fusion and crystallization process. Differential scanning calorimetry was carried out in a Mettler Toledo DSC 822e analyzer. The powder sample (about 30 mg) was taken and used for the DSC measurement. It was heated to 700ºC at a constant heating rate of 50 ºC/min.

3. Results and discussion

3.1. X-ray examination

In order to identify new phases the X-ray examinations were performed. The X-ray analysis to test forming of amorphous phases in mechanical alloying process was used, too.

Figure 2 shows the XRD pattern set of the pure copper powder after 2, 10 and 50 hrs of mechanical milling process. The diffraction patterns of these samples show the peaks characteristic for Cu.

The diffraction records of powders of Nb powder vs. the different time of grinding are shown in Fig. 3.

The diffraction patterns of Nb recorded for the powder after shorter and longer time of milling show the peaks characteristic for Nb. When the milling time increases to 10 hrs all peaks become wider and their intensity decreases. The widening of curves is connected with the size reduction in the powder grains and presence of stresses resulting from the intensive ductile strains occurring during the milling process. The changes of character of background in surroundings of line Nb show the beginning of synthesis of amorphous phase.

Findings of an investigation were presented as diffraction pattern, results of microstresses and crystalline size calculations were set up in Table 3.

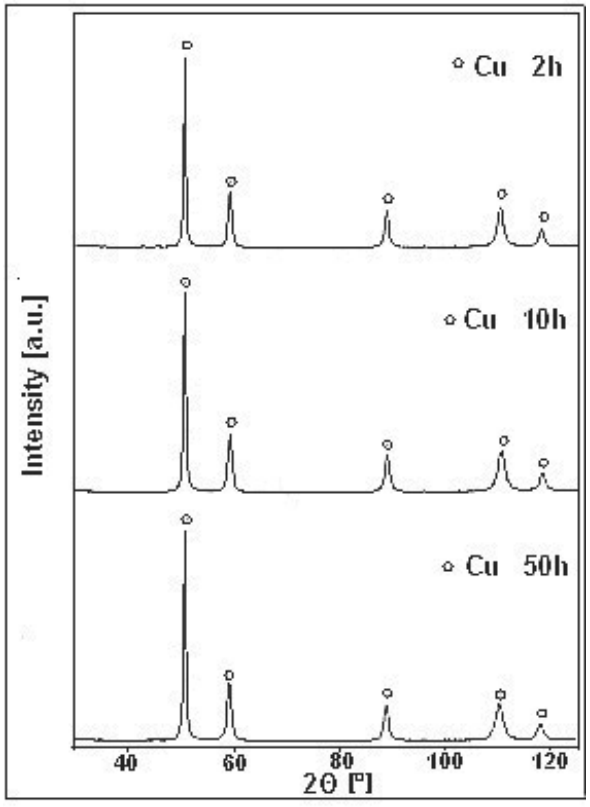

Fig. 2. The X-ray diffraction patterns of Cu powder after 2, 10 and 50 hrs of mechanical milling

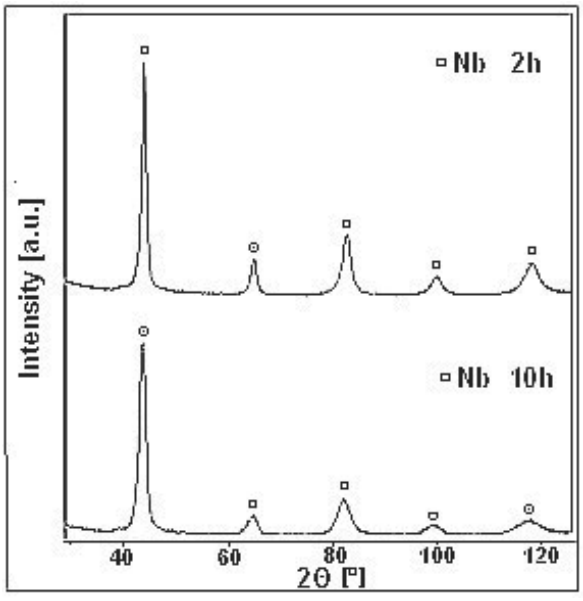

Fig. 3. The X-ray diffraction patterns of Nb powder after 2 and 10 hrs of mechanical milling

Table 3.
Microstresses and crystalline size

	Cu 2h	Cu 10h	Cu 50h	Nb 2h	Nb 10h
D, nm	219	107	72	96	34
< Δa/a >	1390	907	670	3555	5836

The analysis of crystalline sizes and microstresses calculation results allow to maintain that (in all tested samples) the crystalline sizes decrease with the milling time whereas the microstresses value depends on kind of powder material (ductile or brittle).

The microstresses are large in brittle powder. The values increase with the milling time. In the ductile powder the microstresses decrease more after 10 hrs and less and less after 50 hrs of mechanical milling. Probably, this is the result of an influence of material recovery after strain overflow.

The diffraction pattern recorded for the powder ground for 2 hours (Fig. 4.) shows the peaks characteristic for Nb and Sn, whereas none X-ray peak originating from the intermetallic phases was observed.

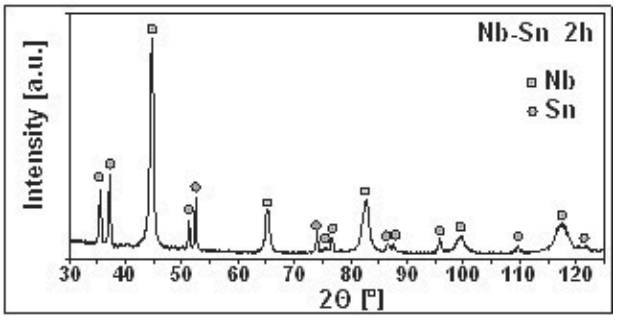

Fig. 4. The X-ray diffraction patterns of Nb 25%at. Sn powder alloy vs. the grinding time 2 hours

The diffraction pattern recorded for the powder of Nb 25%at. Sn powder alloy vs. the mechanical alloying time 10 hours shows the peaks characteristic for Nb, Sn and Nb_3Sn phases. The diffraction record of powder versus the time of grinding is shown in Fig. 5.

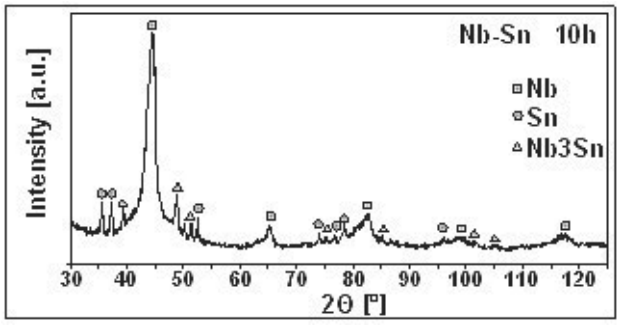

Fig. 5. The X-ray diffraction patterns of Nb 25%at. Sn powder alloy vs. the grinding time 10 hours

3.2. X-ray microanalysis

For better understanding of the mechanical alloying process, the X-ray microanalysis was carried out on the ductile and less ductile powders after 2 and 10 hrs of this process. Nb 25at.% Sn powder alloy was observed in different magnifications. The microstructure of obtained alloy is composed of small particles and quite large agglomerates. The chemical composition of different sites of included powder material was tested. The chemical composition analysis of all samples was carried out by focus electron beam. The microstructure analysis of chosen fragment of Nb-Sn powder alloy after 2 hrs of mechanical alloying is shown in Figs. 6-8.

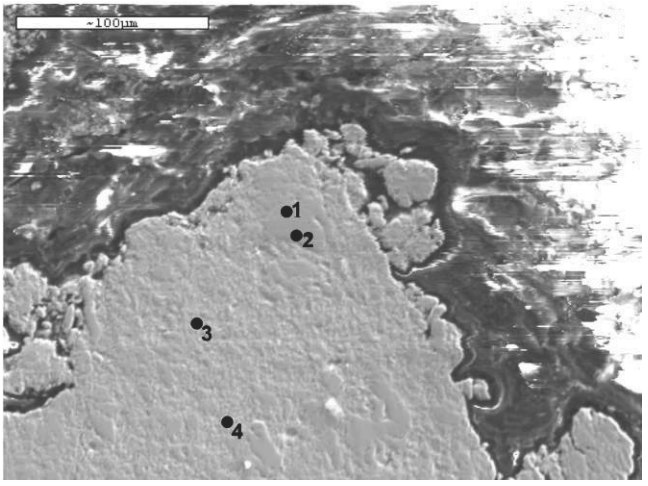

Fig. 6. Surface microstructure of analysed Nb-Sn powder alloy mechanically milled for 2 hrs

The mass concentration of niobium and tin from marked points in Figs. 6-8 are listed in Tables 4-6, adequately.

Table 4.
Chemical composition of marked points in Fig. 6 Nb-Sn alloy after 2 hrs of mechanical alloying process

Point	Element	Mass concentration, %
1	Nb	87.20
	Sn	12.80
2	Nb	81.01
	Sn	18.99
3	Nb	53.64
	Sn	46.36
4	Nb	71.47
	Sn	28.53

The chosen area of analysed Nb-Sn powder alloy mechanically milled for 2 hrs is presented in Fig. 9.

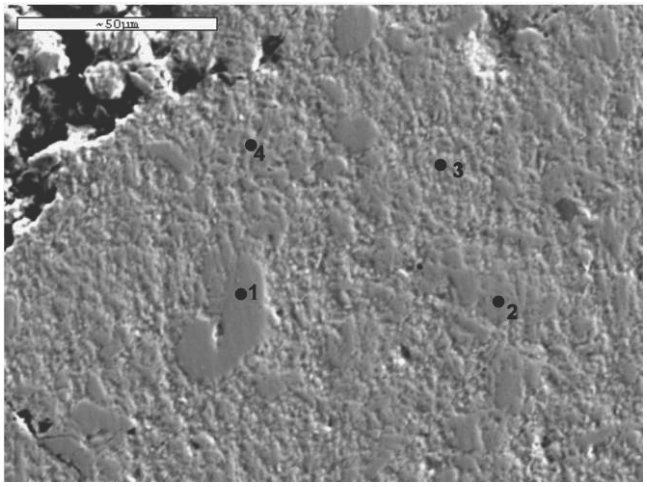

Fig. 7. Surface microstructure of analysed Nb-Sn powder alloy mechanically milled for 2 hrs

Table 5.
Chemical composition of marked points in Fig. 7 Nb-Sn alloy after 2 hrs of mechanical alloying process

Point	Element	Mass concentration, %
1	Nb	62.54
	Sn	37.46
2	Nb	66.85
	Sn	33.15
3	Nb	68.52
	Sn	31.48
4	Nb	55.31
	Sn	44.69

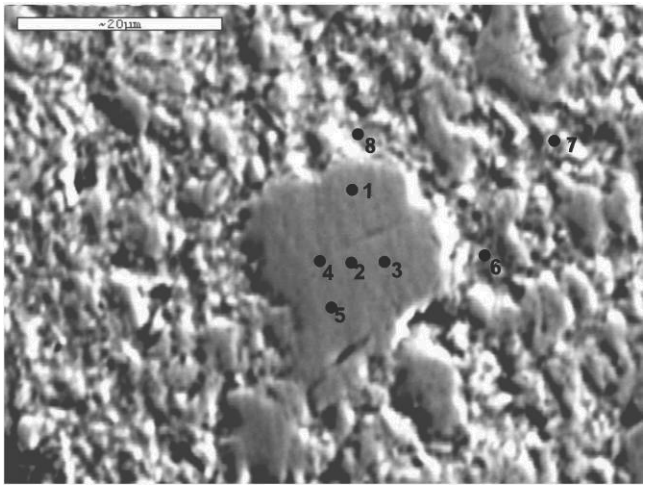

Fig. 8. Surface microstructure of analysed Nb-Sn powder alloy mechanically milled for 2 hrs

The examples of the plots of X-ray dispersive energy measurement from the Nb-Sn alloy after 2 hrs of mechanical alloying are shown in Figs. 10-12.

Table 6.
Chemical composition of marked points in Fig. 8 Nb-Sn alloy after 2 hrs of mechanical alloying process

Point	Element	Mass concentration, %
1	Nb	48.74
	Sn	51.26
2	Nb	57.79
	Sn	42.21
3	Nb	56.89
	Sn	43.11
4	Nb	64.49
	Sn	35.51
5	Nb	61.12
	Sn	38.88
6	Nb	94.67
	Sn	5.33
7	Nb	73.21
	Sn	26.79
8	Nb	55.27
	Sn	44.73

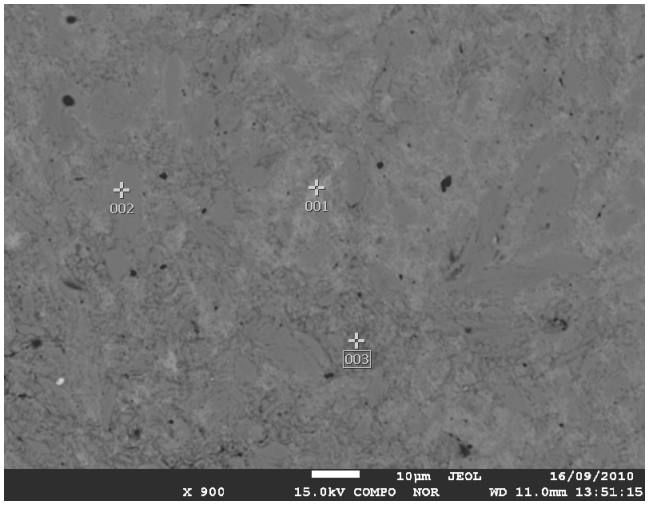

Fig. 9. Microstructure of analysed Nb-Sn powder alloy mechanically milled for 2 hrs

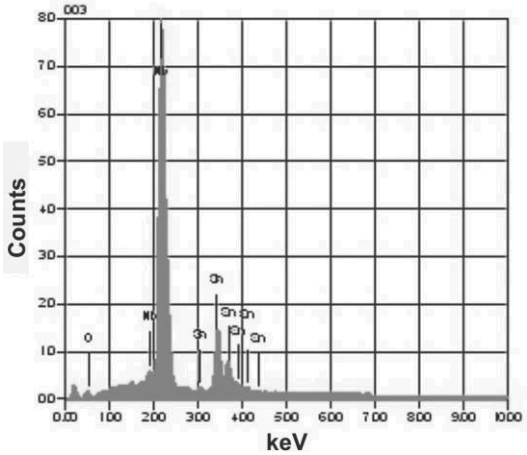

Fig. 10. Plots of the X-ray dispersive energy spectrometer measurement from the Nb 25at.% Sn powder alloy (point [003] in Fig. 9)

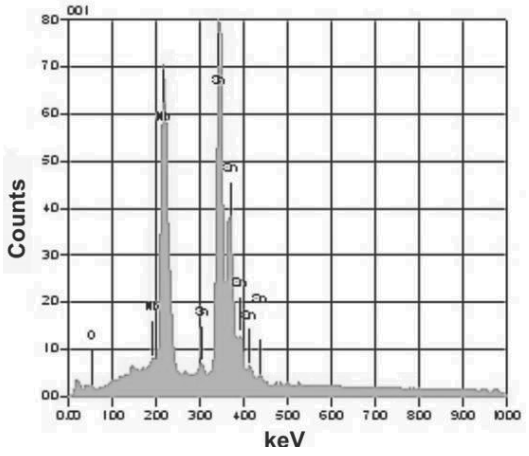

Fig. 11. Plots of the X-ray dispersive energy spectrometer measurement from the Nb 25at.% Sn powder alloy (point [001] in Fig. 9)

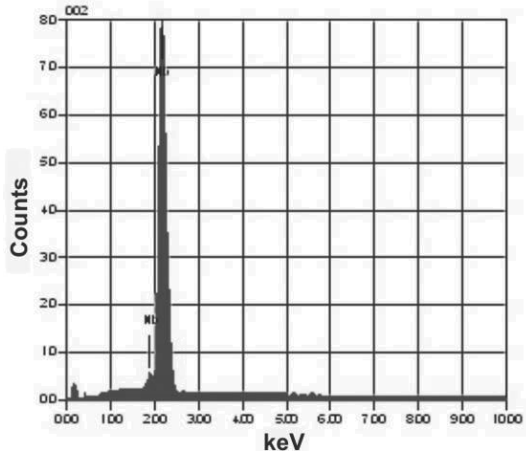

Fig. 12. Plots of the X-ray dispersive energy spectrometer measurement from the Nb 25at.% Sn powder alloy (point [002] in Fig. 9)

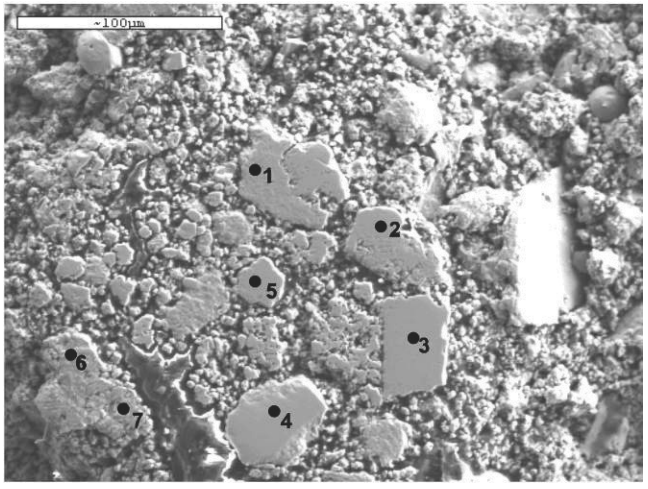

Fig. 13. Surface microstructure of analysed Nb-Sn powder alloy mechanically milled for 10 hrs

The mass concentration of niobium and tin from marked points in Figs. 13-14 are listed in Tables 7-8, adequately.

A little oxygen concentration (2-5 mass.%) was detected in tested material area.

The initial mass concentration of Nb equal 70.13% and Sn 29.87%. The investigation result have shown that the obtained powder particles after 2 hrs of mechanical alloying process are non-homogeneous. However, it can be noticed that during the longer process powder particles are a little more homogenous. The chemical composition of studied areas' powder sample after 10 hrs of mechanical alloying in marked point bears a resemblance to initial chemical composition.

Laboratory test of the chemical composition of the Nb 25at.% Sn indicates that the process has not still come to the end. Laminar powder particle structure does not occur there. Probably, the mechanical alloying process of tested Nb-Sn material should be increased. It depends on the material properties. The mixture of ductile-ductile and brittle-brittle powders maintain different.

Table 7.
Chemical composition of marked point in Fig. 13 Nb-Sn alloy after 10 hrs of mechanical alloying process

Point	Element	Mass concentration, %
1	Nb	99.50
	Sn	0.50
2	Nb	71.64
	Sn	28.36
3	Nb	70.79
	Sn	29.21
4	Nb	99.52
	Sn	0.48
5	Nb	59.82
	Sn	40.18
6	Nb	86.30
	Sn	13.70
7	Nb	85.70
	Sn	14.30

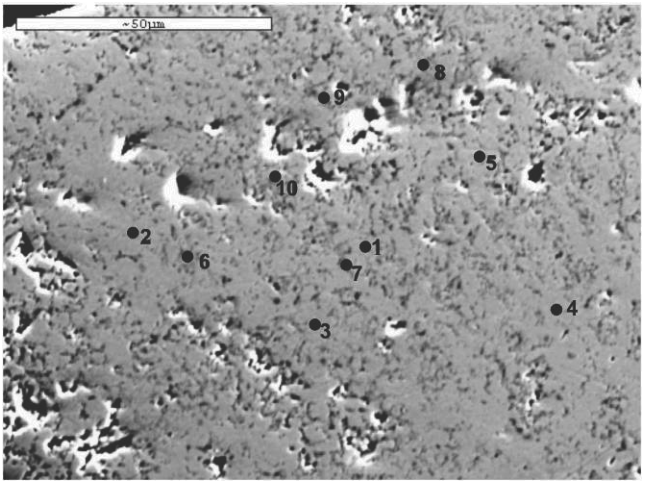

Fig. 14. Surface microstructure of analysed Nb-Sn powder alloy mechanically milled for 10 hrs

Table 8.
Chemical composition of marked points in Fig. 14 Nb-Sn alloy after 10 hrs of mechanical alloying process

Point	Element	Mass concentration, %
1	Nb	70.26
	Sn	29.74
2	Nb	71.61
	Sn	28.39
3	Nb	69.95
	Sn	30.05
4	Nb	96.75
	Sn	30.25
5	Nb	71.69
	Sn	28.31
6	Nb	67.11
	Sn	31.08
7	Nb	66.78
	Sn	28.80
8	Nb	68.69
	Sn	30.43
9	Nb	67.98
	Sn	30.90
10	Nb	69.65
	Sn	29.76

3.3. Results of analysis of the crystallization process

The calorimetric measurements enable to detect energetic changes which occur in powder material during heating to temperature of 700 °C. Fig. 15 shows the fragment of DSC curve of Nb-Sn powder alloy after mechanical alloying process.

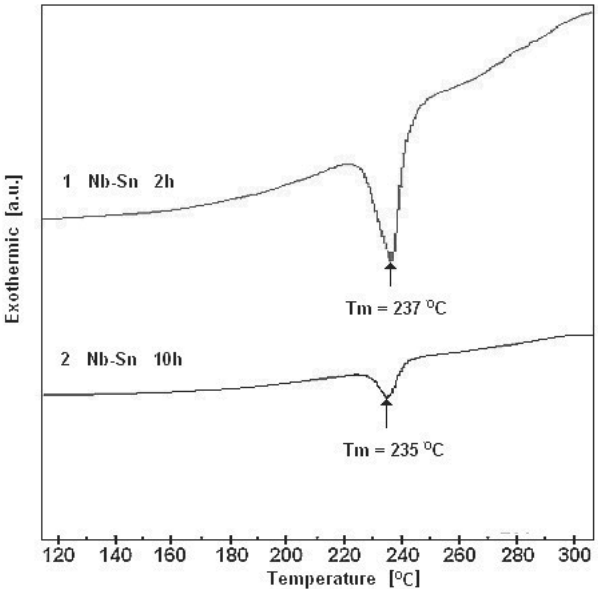

Fig. 15. DSC curve of Nb-Sn powder alloy after 2 hrs and 10 hrs of mechanical alloying

The endothermic effects are visible at Nb 25%at. Sn powder alloy after 2 and 10 hrs of mechanical alloying. The curves recorded for the ground ductile-brittle powders show the distinct endothermic peaks. Probably, they are formed in the consequence of tin melting (Tm – melting temperature).

During the heating of studied 10 hrs milled Nb powder the exothermic peak was formed. Fig. 16 shows DSC curves of Nb powders after 2 and 10 hrs of milling.

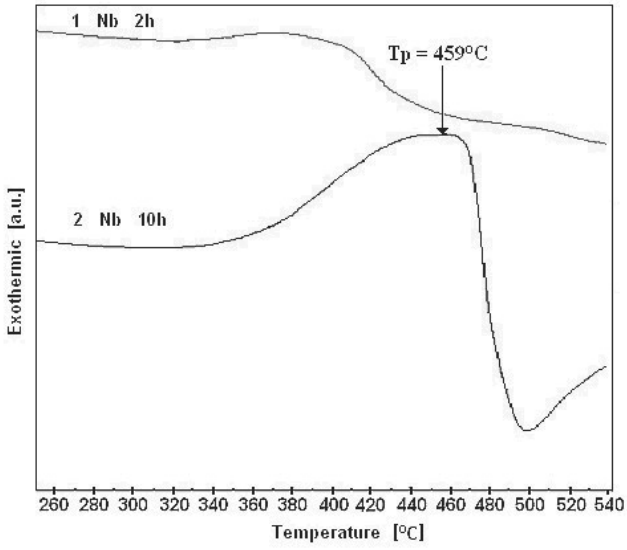

Fig. 16. DSC curve of Nb powder after 2 hrs and 10 hrs of mechanical milling

As research in the previous study, the structural change at the peak 2 is possibly associated with the structural change in the amorphous state during the progress of mechanical milling of Nb powder.

4. Conclusions

The relationship between the initial powder materials properties and mechanical alloying process was specified. The initial powder properties have an influence on the course of mechanical alloying and milling process and the structure of powder.

The ductile and brittle powder particles join and crash during mechanical alloying. Niobium has a BCC structure and is more brittle than tin. During milling, the brittle Nb gets fragmented more easily than Sn and coats surface of the ductile Sn. Probably, the homogeneous structure will be formed as the process is continued.

Results of research show that the crystalline size decrease with the milling time of ductile powder (Cu) and less ductile powder (Nb). An influence of stresses on diffraction pattern broadening decrease with the duration of process.

The test shows that the amorphous structure was obtained in niobium powder after 10 hrs of mechanical alloying whereas there were no amorphous phases in the ductile powder. The exothermic peak in the DTA curve for the mechanically milled for 10 hrs Nb powder corresponds to the peak temperature required to transform amorphous powder Nb to crystalline phase.

Though, from the obtained results, it is clear that mechanical alloying method would ensure complete and near instantaneous transformation of Nb-Sn powder mixture to Nb_3Sn, eliminating the need for independent long duration heat-treatments that are normally required during the processing of Nb_3Sn superconductors.

References

[1] C. Suryanarayana, Mechanical alloying and milling, Progress in Materials Science 46 (2001) 1-184.

[2] G. Matula, L.A. Dobrzański, G. Herranz, A. Varez, B. Levenfeld, J.M. Torralba, Structure and properties of HS6-5-2 type HSS manufactured by different P/M methods, Journal of Achievements in Materials and Manufacturing Engineering 24/1 (2007) 71-74.

[3] L.A. Dobrzański, B. Dołżańska, Structure and properties of sintered tool gradient materials, Open Access Library 1 (2011) 89-132.

[4] L.A. Dobrzański, A. Kloc-Ptaszna, G. Matula, J.M. Contreras, J.M. Torralba, The impast of production methods on the properties of gradient tool materials, Journal of Achievements in Materials and Manufacturing Engineering 24/1 (2007) 19-25.

[5] M. Rosso, D. Ugues, M. Actis Grande, The challenge of PM tool steels for the innovation, Journal of Achievements in Materials and Manufacturing Engineering 18 (2006) 175-178.

[6] G. Matula, Carbide alloyed composite manufactured with the PIM method, Archives of Materials Science and Engineering 43/2 (2010) 117-124.

[7] P. Klimczyk, V.S. Urbanovich, Micro-, submicro- and nano-Si_3N_4-SiC composites sintered by the HPHT method, Archives of Materials Science and Engineering 39/2 (2009) 92-96.

[8] I. Sulima, P. Klimczyk, P. Hyjeka, The influence of the sintering conditions on the properties of the stainless steel reinforced with TiB_2 ceramics, Archives of Materials Science and Engineering 39/2 (2009) 103-106.

[9] M. Czepelak, M. Staszewski, A. Wrona, M. Lis, M. Osadnik, Fabrication of nano-structured materials by high-pressure sintering, Archives of Materials Science and Engineering 30/2 (2008) 109-112.

[10] L.A. Dobrzański, M. Kremzer, M. Adamiak, The influence of reinforcement shape on wear behaviour of aluminium matrix composite materials, Journal of Achievements in Materials and Manufacturing Engineering 42 (2010) 26-32.

[11] M. Jurczyk, Mechanical Alloying, Published by Poznan University of Technology, Poznan, 2003 (in Polish).

[12] W. Pilarczyk, R. Nowosielski, A. Pilarczyk, The structural study of Ti-Si-C alloys produced by mechanical alloying method, Archives of Materials Science and Engineering 38/2 (2009) 78-84.

[13] W. Pilarczyk, R. Nowosielski, A. Pilarczyk, P. Sakiewicz, A production attempt of $Ni_{50}Ti_{50}$ and $Ni_{52}Ti_{41}Nb_7$ alloys by mechanical alloying method, Archives of Materials Science and Engineering 47/1 (2011) 19-26.

[14] W. Pilarczyk, R. Nowosielski, M. Nowak, M. Kciuk, The structural changes of Al-Ti-Fe alloy during mechanical alloying process, Journal of Achievements in Materials and Manufacturing Engineering 29/2 (2008) 131-138.

[15] V. Kevorkijan, S.D. Škapin, Fabrication and characterization of TiAl/Ti_3Al-based intermetallic composites (IMCs) reinforced with ceramic particles, Archives of Materials Science and Engineering 40/2 (2009) 75-83.

[16] W. Pilarczyk, R. Nowosielski, M. Jodkowski, K. Labisz, H. Krztoń, Structure and properties of $Al_{67}Ti_{25}Fe_8$ alloy obtained by mechanical alloying, Archives of Materials Science and Engineering 31/1 (2008) 29-32.

[17] L. Lü, M.O. Lai, S. Zhang, Modeling of the mechanical alloying process, Journal of Materials Processing Technology 52 (1995) 539-546.

[18] J.B. Fogagnolo, F. Velasco, M.H. Robert, J.M. Torralba, Effect of mechanical alloying on the morphology, micro-structure and properties of aluminium matrix composite powders, Materials Science and Engineering A 342 (2003) 131-143.

[19] M. Szymczak, The influence of initial powder properties on the mechanical alloying process and the properties of final powders, Diploma Work, 2010 (in Polish).

[20] S.N. Patankar, F.H. Froes, Formation of Nb_3Sn using mechanically alloyed Nb-Sn powder, Solid State Sciences 6 (2004) 887-890.

[21] F.A. Santos, A.S. Ramos, C. Santos, D. Rodrigues Jr., Obtaining and stability verification of superconducting phases of the Nb-Al and Nb-Sn systems by mechanical alloying and low-temperature heat treatments, Journal of Alloys and Compounds 491 (2010) 187-191.

[22] Ý. Erdem, H. Hüseyin Kart, T. Cagin, First principles studies of SnO at different structures, Archives of Materials Science and Engineering 45/2 (2010) 108-113.

[23] H. Adrian, K. Spiradek-Hahn, The simulation of dendritic growth in Ni-Cu alloy using the phase field model, Archives of Materials Science and Engineering 40/2 (2009) 89-93.