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MECHANICAL ALLOYING IN PLANETARY MILLS OF HIGH ACCELERATIONS

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Abstract. Mechanical activation effects were studied for metal matrix composites (MMC). Planetary mills of high accelerations were applied in super-high energy milling with the aim of obtaining an Aluminium alloy AA6061 containing a finely dispersed hard phase of NiTi or Al_2O_3. During separate milling of the components it was possible to diminish the particle size and obtain a narrow particle size distribution. The crystallite size attained for Al alloy can be as low as 40 nm. The time of milling in the planetary mills of 28 and 50 g accelerations is much lower than that in the milling devices of lower energy density. During the process of mechanical alloying in the planetary mill further reduction of the crystallite size took place, yielding nanoscale crystallite size for all components. A high degree of coverage of the reinforcement particles by aluminium was achieved. A sample of NiTi mechanically alloyed with AA6061 showed excellent matrix/particle interface and low porosity in the MMC powder. Fine dispersion of NiTi particles was obtained, and the reinforcement particles were well distributed in the matrix. The use of planetary mills of high accelerations can significantly accelerate mechanical alloying.

1. INTRODUCTION

The quest for new aluminium alloys of better performance has been in progress at least since the discovery of practical methods for producing aluminium itself. Almost from the beginning, the usefulness of such alloys in high performance aerospace structures was recognized, and research aimed at identifying alloys and processes producing unique combinations of mechanical and physical properties has been ongoing since that time [1]. In this work the following two approaches, using mechanical activation, are investigated to improve the performance of commercially used Al alloys.

1. Nanocrystalline materials with grain sizes of the order of 100 nm and below are known to be high-strength materials, with the yield strength of about an order of magnitude higher than that for their coarse-grained counterparts [2]. It has been shown recently that nanocrystalline metals and alloys can be produced by mechanical treatment. This method introduces large deformations into the material and produces nanocrystalline structure by creating randomly orientated high-angle grain boundaries within conventional polycrystals [3]. Our motivation was to obtain nanocrystalline commercial Al alloys by ball milling without using liquid nitrogen for cooling.

2. Metal matrix composites possess the metallic properties of ductility, toughness and environmental resistance in combination with the ceramic properties of high strength and high modulus. The widely used commercial particulates generally have a size ranging from a few micrometers to several

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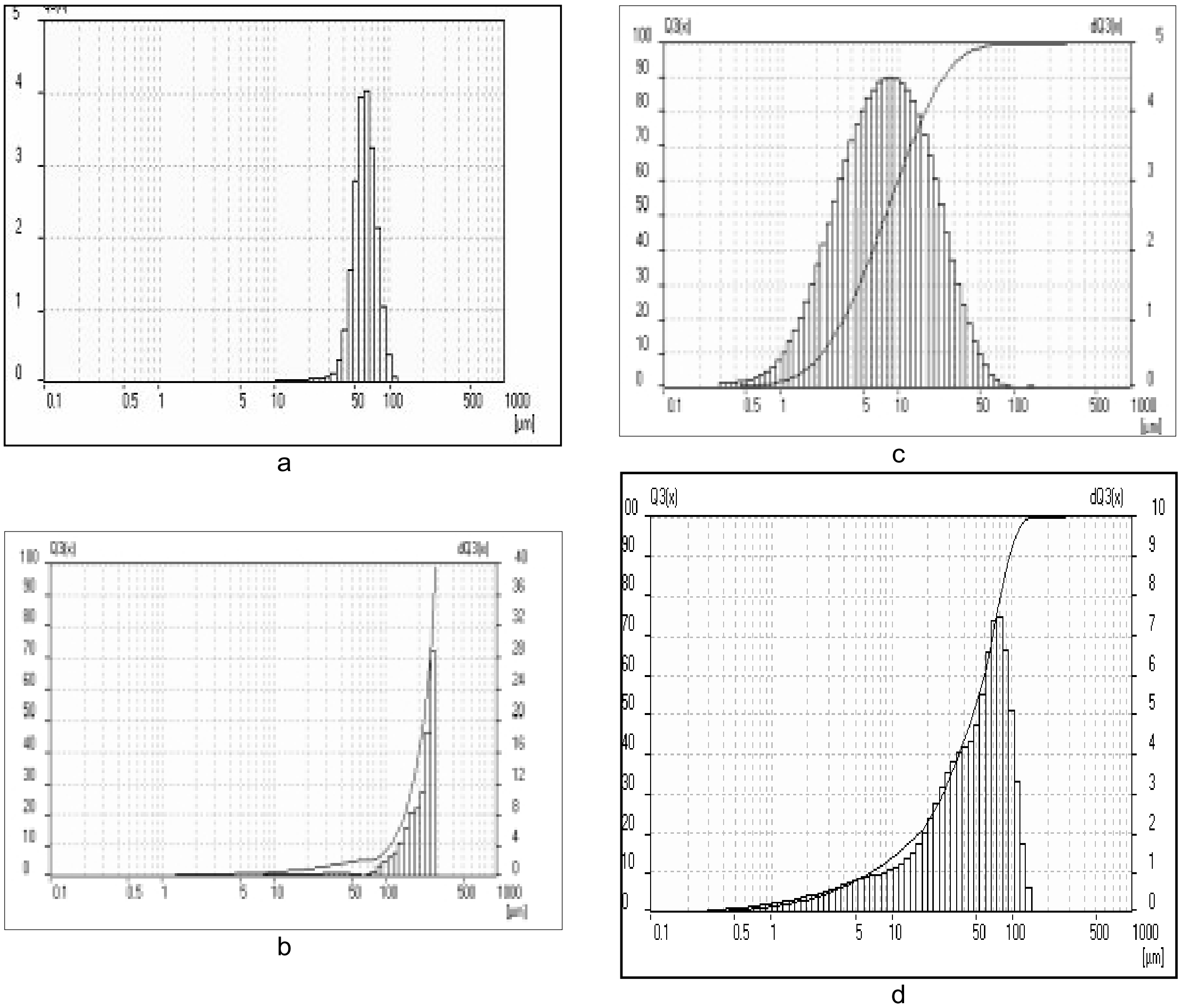

Fig. 1. Particle size distribution for Al alloy AA6061: a) initial; b) milled in Pulverisette 6 mill in Ar at 6.5 g for 4 h; c) milled in MPP-1 mill in air at 28 g for 30 min; d) milled in MPP-1-1 mill in Ar at 50 g for 20 min.

hundred micrometers. Some investigations have indicated that the strength of the composites tends to increase with decreasing particulate size. Therefore nanometric particulates have attracted considerable attention for their special properties [4]. High energy ball milling was successfully employed to fabricate metal matrix composites (MMCs) [5]. Liquid phase processes result in the lower values of the mechanical properties because of bad wetting of the particles [6].

It is known that planetary mills possess higher energy density and provide stronger mechanical impact on materials than other milling devices. Planetary mills are characterized by higher pressure on particles and higher energy density than attritors, vibro-mills, jet mills and disintegrators [7]. Earlier only laboratory planetary mills were in use, and at present industrial planetary mills are commercially available [8]. Industrial planetary mills of periodic action characterized by acceleration of 20 g (1 g is gravitational acceleration) and productivity up to 20-40 kg/h are promising for applications in powder metallurgy. The aim of the present work was to perform comminution and mechanical alloying and study possibilities of the laboratory planetary mills of high accelerations having in mind that scaling up of the processes is possible.

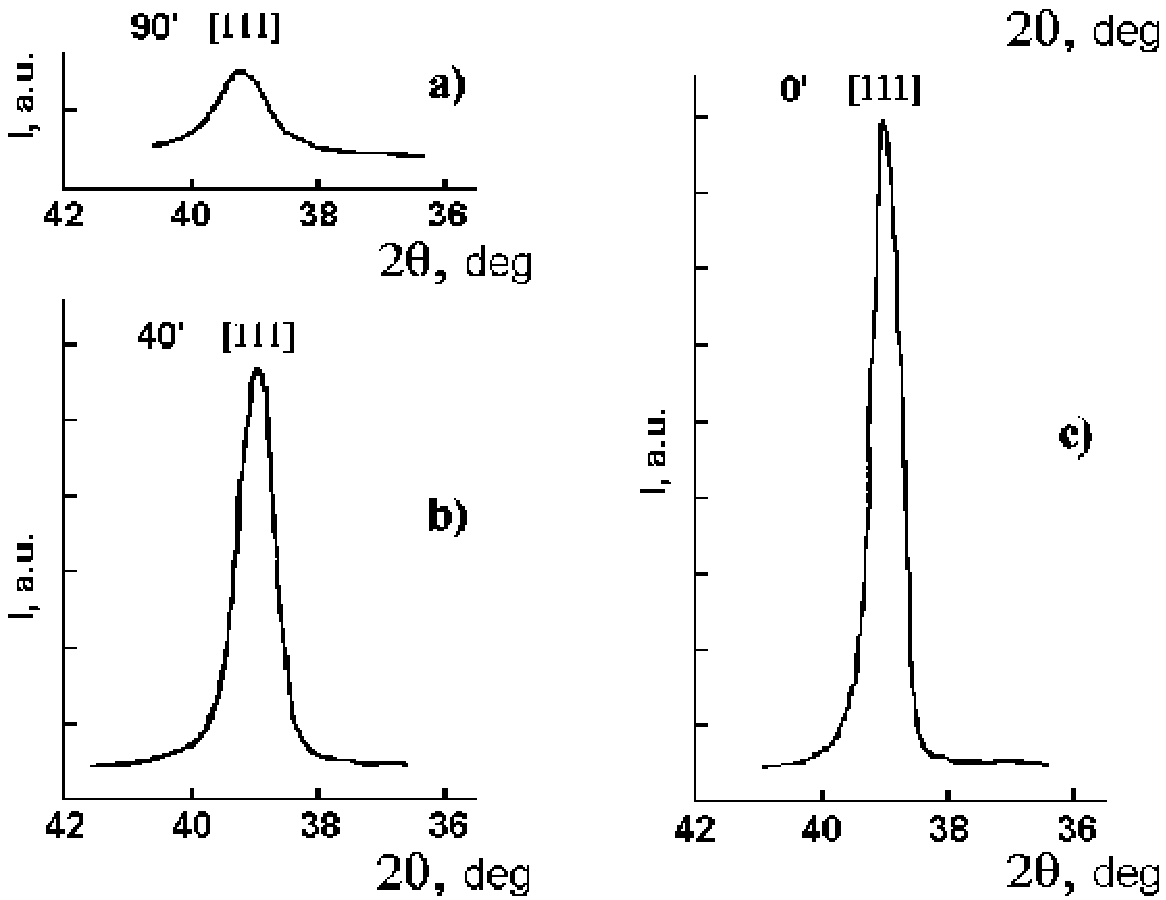

Fig. 2. Comparison of X-ray diffraction [111] maximum of Al alloy AA6061 samples - powder milled at acceleration 28 g for 90 min (a), powder milled for 40 min (b) and initial powder (c).

2. EXPERIMENTAL

Materials

Aluminium powder AA6061 was produced by intergas spray-atomization at ECKART-WERKE (Fürth, Germany). ASM specifications allow the following content of elements: Al – balance, Mg 0.8-1.2%, Si 0.4-0.8%, Cu 0.15-1.4%, Cr 0.04-0.35%, Fe 0.7%. The particle size of the initial powder was reported to be 50-100 μm. Al_2O_3 micropowder, particle size 100-400 μm, was manufactured by Abler (Germany) and NiTi powder was supplied by NANOVAL (Berlin, Germany), Ni:Ti ratio = 50:50, particle size 45 - 350 mm.

Milling conditions

Mechanical milling was performed at the Corporate Research Centre of the European Aeronautic Defence and Space Company (EADS) in the following milling device: planetary ball mill Pulverisette 6 (Fritsch, Germany). The vial and the balls (10 mm diameter) are made up of hardened steel. The ball-to-powder ratio was 5:1. A rotational speed of 250 rpm results in an acceleration of about 6.5 g. Milling with the use of Pulverisette 6 planetary mill was accomplished inside an Ar filled glove box. To avoid temperatures >60 °C the process was stopped for 45 min after 15 min milling. Milling was performed for 1, 4, 8, 16, and 64 h.

The possibilities of the planetary ball mills [8] produced by Technics and Technology of Disintegration Ltd. (TTD, Russia) were investigated. The planetary mills of periodic action (MPP) of this manufacturer are characterized by high acceleration of 25 g and higher [9]. Laboratory planetary mills MPP-1 (at acceleration 28 g) and MPP-1-1 (acceleration 50 g) with steel jars and milling bodies were exploited. Milling experiments at high accelerations were performed at the TTD company.

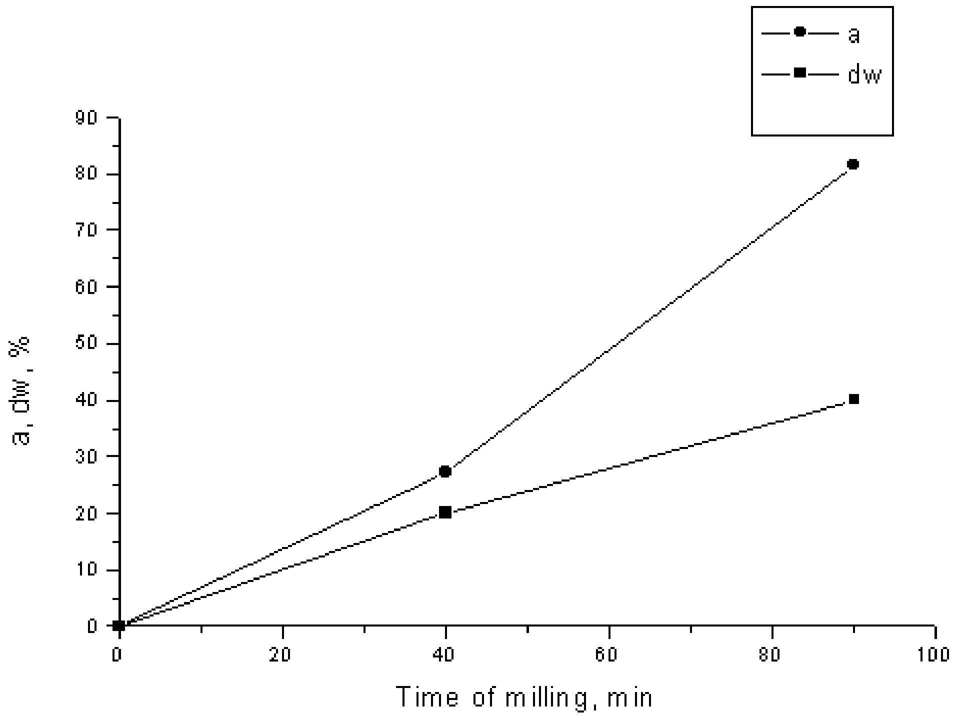

Fig. 3. Dependence of the degree of amorphisation (a) and structural factor (*dw*) calculated from X-ray data for AA6061 upon time of milling in air at acceleration 28 g.

The technical specifications of MPP-1 mill are given in Table 1. The milling of NiTi was performed at 50 g, with removing of the finest fraction and adding of the initial powder after 5 min milling. The total time of the milling experiments was 88 min for milling in air and 160 min for milling in jars filled with argon. Al_2O_3 was milled in air at 50 g for 5 min.

Methods

Scanning electron microscope (SEM) observations were performed by means of JEOL JSM-6320F. X-ray diffraction analysis was performed at St. Petersburg State University using DRON 4 M (Burevestnik, Russia) X-ray diffractometer, CuK_α radiation, Ni filter. Emission spectroscopy analysis was done by means of a DFS-13 spectrophotometer (Russia) in order to estimate the contents of elements in the subject matter. TEM observations were carried out with a Philips CM20 microscope operated at 200 kV at the University of Erlangen. The determination of the particle size was carried out by means of laser diffraction using "Analysette 22" (Fritsch, Germany).

3. RESULTS AND DISCUSSION

Milling of Al alloy AA6061

Milling of AA6061 in planetary mills of different accelerations was undertaken with the aim to diminish the crystallite size. Particle size distribution for the initial and milled powders is reproduced in Fig. 1. Milling at acceleration of 6.5 g induced particle growth because of strong cold welding tendencies (Fig. 1b). The particle size increased from 50 μm to about 1500 μm in the milling time of more than 4 h. Particles milled for a duration longer than 4 h exhibited an almost spherical morphology. The average crystallite size was found to be less than 100 nm.

After milling in TTD planetary mill MPP-1 at an acceleration of 28 g the diminishing of the particle size was achieved. The average particle size d_{50} observed after 30 min milling was 7.5 μm. The size distribution curve of a sample ground for 30 min was rather narrow (Fig. 1c). For that sample 10% of the particles had sizes less than 2 μm. Contamination as a result of grinding was rather small

Table 1. Technical specifications of MPP-1 planetary mill of periodic action (TTD, Russia) [13].

PARAMETERS	MODEL MPP-1
Number of jars	4
Jar diameter, mm	Changeable jars 80, 100, 120, 150
Jar height, mm	48
Single jar volume, without lining, ml	variable 240; 370; 540; 850
Loaded batch volume per jar, ml	variable 40; 70; 100; 170
Weight of the loaded material of density 3 g/cm^3, g	variable
- per jar	120; 210; 300; 510
- per all jars	480; 840; 1200; 2040
Maximum particle size of feed material, mm	2
Milling time, min	
- till 90% less than 10 μm	5 ÷ 10
- till 90% less than 1 μm	20 ÷ 40
Centrifugal factor, *G* (gravitational acceleration)	Variable, up to 25
Electric motor, asynchronic 3-phasic	
Nominal power, kW	3.0
Weight, kg	130
Dimensions, *L*x*B*x*H*, m	0.7 x 0.5 x 0.4

(0.05% of Fe for 30 min milling), and the acceptable values of Fe content were not exceeded.

The diminished height and broadening of the peaks in the X-ray diffraction data for Al alloy powder that was activated for 40 and 90 min at 28 g revealed a remarkably strong amorphisation of the structure (Fig. 2). The amorphisation degree (a), the size of the regions of coherent scattering (crystallite size) and the structural factor (dw) were calculated according to the technique described earlier [10]. The structural factor reflects the accumulation of various types of defects of the crystalline structure in the state that is pre-transitional to the X-ray-amorphous structure. The crystallite size reduces to 38 nm after 90 min milling (Table 2). Both the amorphisation degree and the structural factor grow drastically with the milling duration (Fig. 3). The values of the crystallite size of ground AA6061 powder determined by electron microscopy were consistent with the data calculated from X-ray diffraction patterns.

Summarizing these findings, in the TTD mill MPP-1, with an acceleration four times higher (28 g) than in the reference planetary ball mill, a smaller grain size of 38 nm was achieved almost 5 times faster. It has been made clear that the milling time for grain size refinement could be drastically reduced when the acceleration of the mill is enhanced.

Al alloy AA6061 was milled in a TTD planetary mill MPP-1-1 at an acceleration of 50 g for 22.5 min (in 2.5 min increments) with metal balls in air and for 20 min in Ar atmosphere. The particle size distribution given in Fig. 1, d reveals significant amounts of small particles. The crystallite sizes for these samples were found to be 73 nm and 70-80 nm, respectively (Table 2). The alloy particles exhibited flake-like shape, which was found to be an advantage for further processing. The element content of AA6061 samples obtained by milling at an acceleration of 50 g showed that the content of Fe and Cr stayed within the limits defined by ASM specifications.

Milling of reinforcements

NiTi powder was milled at an acceleration of 50 g in small increments, removing (-40) μm fraction and

Table 2. Crystallite size calculated from X-ray diffraction data for Al alloy AA6061 and reinforcements milled in planetary mills. Comparison with literature data for Al milled in attritor and in SPEX 8000 mill.

Milling equipment	Acceleration, atmosphere	Time of milling	Crystallite size
	AA6061		
TTD planetary mill MPP-1	28 g, air	40 min	130 nm
TTD planetary mill MPP-1	28 g, air	90 min	38 nm
TTD planetary mill MPP-1-1	50 g, air	22.5 min	73 nm
TTD planetary mill MPP-1-1	50 g, Ar	20 min	70-80 nm
Fritsch planetary mill Pulverisette 6	6.5 g, Ar	8 h	<100 nm
	Al		
Al - Attritor [11]	liquid N_2	16 h	26 nm
Al - SPEX 8000 [12]	Ar	24 h	22 nm
	NiTi		
TTD planetary mill MPP-1-1	50 g, Ar	160 min	< 50 nm
	Al_2O_3		
TTD planetary mill MPP-1-1	50 g, air	5 min	100 nm

Table 3. Crystallite sizes and coverage degree of reinforcement calculated from X-ray data for Al alloy AA6061 and Al_2O_3 mechanically alloyed at acceleration 28 g for 10 and 15 min.

Mechanical alloying time, min	Al crystallite size, nm	Al_2O_3 crystallite size, nm	Al_2O_3 coverage degree, %
0	70	100	
10	60	80	97
15	50	80	97.5

adding raw powder, in total for 88 min in air and another sample for 160 min in Ar. The crystallite size after milling for 160 min was found to be less than 50 nm. The particles were found to have flat shape. Al_2O_3 was milled at TTD at 50 g for 5 min with metal balls in air atmosphere, with 100 nm crystallite size obtained.

4. PREPARATION OF METAL MATRIX COMPOSITES

Al alloy AA6061/Al_2O_3 composite

Alloy AA6061 pre-milled at 50 g for 20 min and Al_2O_3 pre-milled in air at 50 g for 5 min were used for the preparation of metal matrix composite. Mechanical alloying was performed in Ar atmosphere for the batch containing 10 vol.% Al_2O_3 at an acceleration of 28 g during 5, 10, and 15 min. It can be seen from the X-ray diffraction pattern that peaks corresponding to Al_2O_3 have almost completely disappeared in the X-ray pattern for the AA6061/Al_2O_3 composite (Fig. 4). These results indicate a high degree of coverage of Al_2O_3 particles by the Aluminium alloy. Crystallite size values were calculated basing on the X-ray structural analysis results (see Table 2).

As described above, the diminishing of the crystallite sizes of Al and Al_2O_3 takes place when they

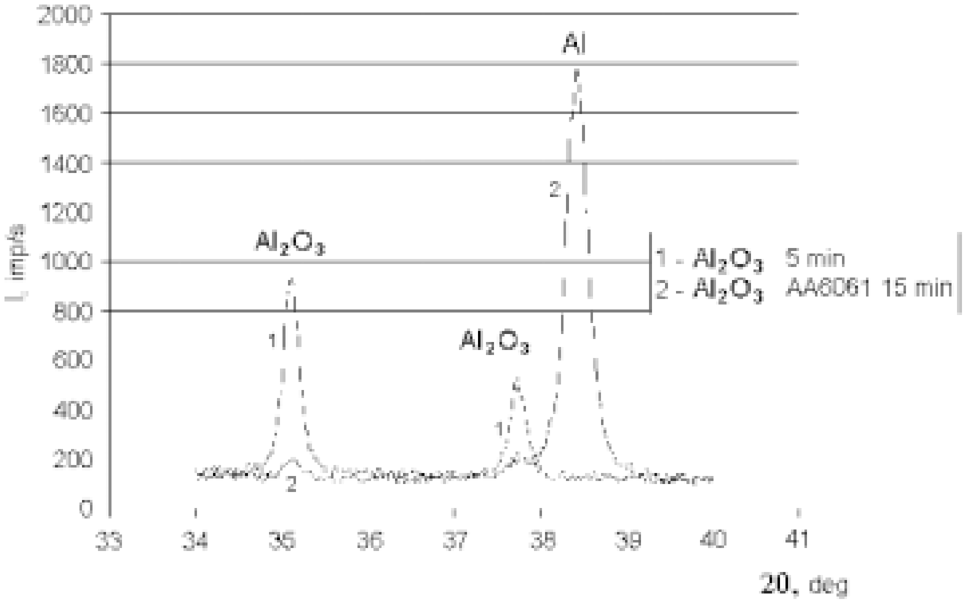

Fig. 4. X-ray diffraction pattern for Al_2O_3 milled in air at 50 g for 5 min (curve 1) and composite AA6061/Al_2O_3 mechanically alloyed in Ar atmosphere at acceleration 28 g for 15 min (curve 2).

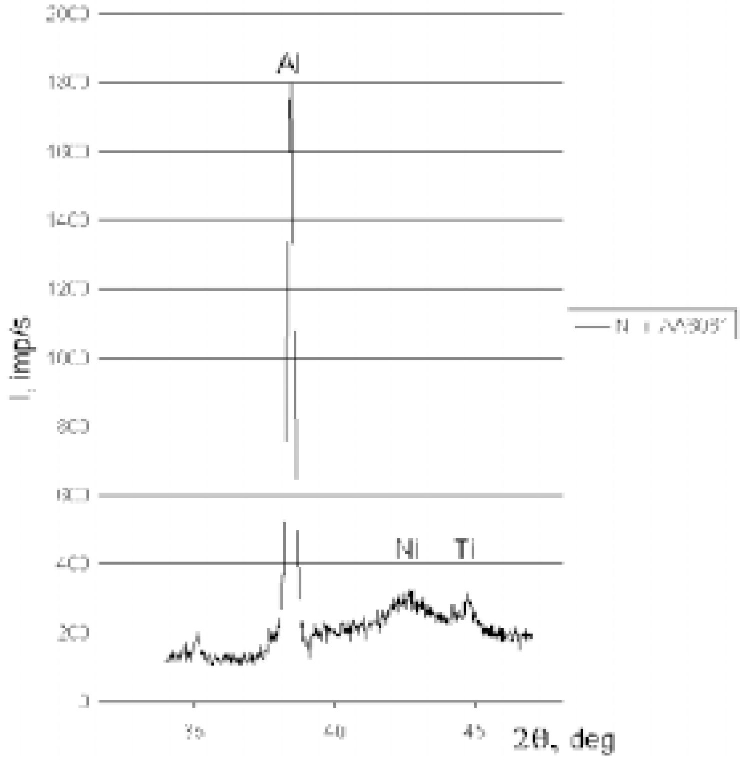

Fig. 5. X-ray diffraction pattern for AA6061/NiTi composite (components pre-milled separately at acceleration 50 g) mechanically alloyed in Ar at acceleration 28 g for 10 min.

are milled separately (at 50 g). Furthermore, during the process of mechanical alloying in the planetary mill at an acceleration of 28 g further reduction of crystallite size is going on, as well as the encapsulation of Al_2O_3 particles with Al alloy. The coverage degree of Al_2O_3 particles was determined according to E. L. Fokina's technique based on the determination of the optical path depth of X-rays in various materials; the data are presented in Table 3. A high degree of coverage of the reinforcement particles by Aluminium (97.5 %) was observed.

Al alloy AA6061/ NiTi composite

Aluminium alloy AA6061 pre-milled at 50 g for 20 min in Ar atmosphere and NiTi pre-milled at 50 g during 88 min were used. A batch containing 10 vol.% NiTi was mechanically alloyed in the TTD planetary mill MPP-1 at 28 g during 5, 10 and 15 min. In Fig. 5 a fragment of an X-ray pattern taken for the composite AA6061/NiTi mechanically alloyed for 10 min is reproduced. A strong amorphization of NiTi can be observed. Both powders show crystallite size in the nanoscale range. As a result of mechanical alloying at an acceleration of 28 g reinforcement particles are coated with Al alloy, which is beneficial for the good distribution in the metal matrix.

This pre-alloyed at 28 g for 15 min NiTi+AA6061 powder was used for further mechanical alloying for 4 h with the initial AA6061 by means of conventional milling at low acceleration (Pulverisette 6, acceleration 6.5 g). It seems that the Al alloy coating on the surface of the NiTi particles improved the adhesion of the initial AA6061 powder (Fig. 6). The micrographs show that the particle-matrix interface is very good irrespective of the size of the reinforcement particles. As the layers of the matrix material on the surface of the NiTi particles are rather thin, these particles could easily be distributed in the initial AA6061 powder by a subsequent milling process. This indicates that pre-alloying at high accelerations activated the powders and provided a second phase that could easily be introduced into the metal matrix.

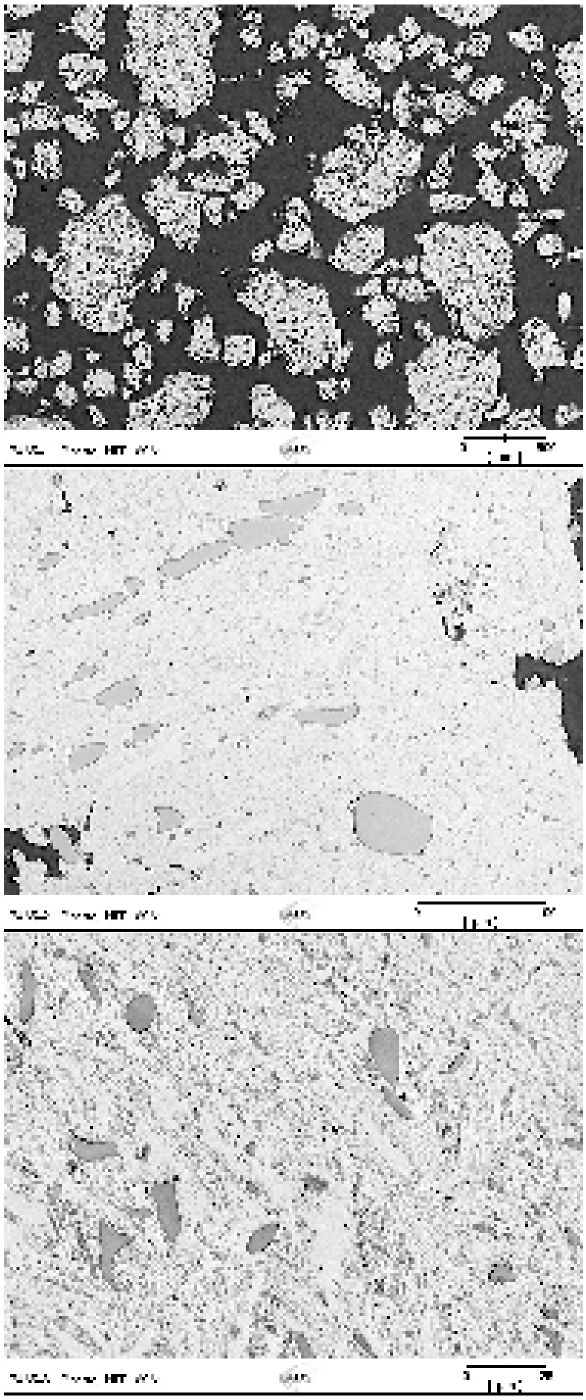

Fig. 6. Image of AA6061+NiTi composite, with components pre-milled separately at 50 g, mechanically alloyed at 28 g for 15 min and additionally mechanically alloyed with initial AA6061 at 6.5 g for 4 h.

5. CONCLUSIONS

The influence of the centrifugal factor was studied for the process of metal matrix composite preparation. The separate milling of the powders of the Aluminium alloy AA6061 and reinforcements NiTi and Al_2O_3 and the mechanical alloying of these components were performed in the planetary mills of different accelerations.

It was demonstrated that during milling of Al alloy in the TTD planetary mill at an acceleration of 28 g for only 30 min it was possible to diminish particle size down to 8 mm and to obtain a narrow particle size distribution. The milling time in the planetary mill of 28 g acceleration is much lower than in milling devices of lower energy density. The crystallite size attained can be as low as 40 nm. The milling time needed to achieve a crystallite size of the nanometer scale in planetary mills of high accelerations is significantly lower compared to the values reported in the literature for milling in an attritor and in a SPEX mill (Table 2).

The milling of Al alloy in the TTD planetary mill of 50 g acceleration in Ar atmosphere resulted in obtaining a crystallite size in the nanoscale region in only 20 min. The milling of reinforcement particles of NiTi required 88-160 min; flat flake-like shape of the particles was beneficial for embedding of the reinforcements in the metal matrix.

The mechanical alloying of AA6061/NiTi and AA6061/Al_2O_3 metal matrix composites (with premilled components) was performed in the planetary mill at 28 g for only 15 min. During the process of mechanical alloying the further reduction of crystallite size took place, yielding nanoscale crystallite size for all the components. The encapsulation of reinforcement particles with Al alloy was revealed. A high degree of coverage (97.5%) of the reinforcement particles by the Aluminium alloy was achieved. Subsequent mechanical alloying at low acceleration (6.5 g) for 4 h resulted in homogeneous distribution of NiTi reinforcements in the matrix and in a good connection to the matrix.

Thus, fast mechanical alloying at an acceleration of 28 g of the components activated at a higher acceleration provided metal-coated particles which could be easily distributed in the metal matrix by a subsequent milling process. Therefore, planetary mills of high accelerations can substantially reduce the time of production of nanocrystalline metal matrix composites.

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REFERENCES

[1] R. R. Sawtell and C.L. Jensen // *Metallurgical Transactions. A* **21A** (1990) 421.
[2] E. Hellstern, H.J. Fecht, Z. Fu and W.L. Johnson // *J.Appl Phys.* **65** (1989) 305.
[3] H.J. Fecht, E. Hellstern, Z. Fu and W.L. Johnson // *Adv. Powder Metall.* **1** (1989) 11.
[4] Z.Y. Ma, Y.L. Li, Y. Liang, F. Zheng, J. Bi and S.C. Tjong // *Mater. Sci. Engineering A* **219** (1996) 229.
[5] M.S. El-Eskandarany // *J. Alloys Compounds* **279** (1998) 263.
[6] A. Malchere, M. Grosbras, D.L. Demenet, L. Bresson and E. Gaffet // *Materials Science Forum* **225-227** (1996) 763.
[7] M.V. Chaikina, *Mechanochemistry of Natural and Synthetic Apatites* (Novosibirsk, 2002), In Russian.
[8] V.G. Kochnev, *Planetary mill*, *RU Patent 1358990* (1992).
[9] E.L. Fokina, N.I. Budim, V.G. Kochnev and G.G. Chernik // *J. Mater. Sci.* **39** (2004) 5217.
[10] A.N. Streletskii, V.I. Lapshin and E.L. Fokina // *Kinetika i kataliz* **30** (1989) 1064, In Russian.
[11] F. Zhou, J. Lee, S. Dallek and E.J. Lavernia // *J. Mater. Res.* **16** (2001) 3451.
[12] J. Eckert, J.C. Holzer, C.E. Krill and W.L. Johnson // *Materials Science Forum* **88-90** (1992) 505.
[13] www.ttd.spb.ru