STUDY OF CHARACTERISTICS OF Al + 5 wt.% TiO_2 + 6 wt.% Gr HYBRID P/M COMPOSITE POWDERS PREPARED BY BALL MILLING PROCESS

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This paper is an attempt to understand the characteristics of Al + TiO_2 + Gr hybrid ball milled composite powders, which is anticipated to have large application in the near future. Aluminium with titanium dioxide (TiO_2) and graphite (Gr) powders was ball milled in order to yield the composition like: Al + 0% TiO_2, Al + 5% TiO_2, Al + 5% TiO_2 + 2% Gr, Al + 5% TiO_2 + 4% Gr and Al + 5% TiO_2 + 6% Gr. From the X-Ray diffraction analysis of the milled powders, the grain size, lattice space, lattice constant, stress, strain, dislocation density and unit cell volume were calculated. Compressibility was performed in a hardened steel die at pressures between 100 to 500 MPa to determine Al with 5 wt.% TiO_2 and 2 & 4 wt.% of Gr powder mixtures. For understanding of compaction behavior of aluminum based hybrid composites reinforced with TiO_2 and Gr particles under various applied pressure conditions, experimental research has been made using several powder compaction equations. Microstructure analysis for Al + 5% TiO_2 + 6% Gr composite has been reported.

Key words: *ball milling, synthesis, composite powders, ball milling.*

Aluminum matrix composites are used for various applications in aerospace, automobile, military and electronic industry due to their low density, high toughness, good mechanical properties and high corrosion resistance [1]. Many varieties of reinforcements are used to produce the aluminium matrix composites. Instead of all, the titanium-di-oxide (TiO_2) also found as a good one, since it has high hardness, high modulus, and wear resistance [2]. Adding of single reinforcement to the matrix material improves the strength and hardness of the material, but it leads to the machining problem [3]. Recently aluminum alloy–graphite particulate composite is being used in various applications because of its low friction and wear, improved machinability, low thermal expansion and high damping density [4]. In this work both the hard TiO_2 and soft graphite powders are used as reinforcements to produce the aluminium hybrid composites and it is expected to be used for various application. The mechanical alloying process is used to produce the advanced composite materials [5]. Mechanical alloying is a widely used technique in synthesizing nanocrystalline materials and also it has been used to prevent the reinforcement clusters or agglomerates on the matrix, especially in the case of small size reinforcement particles that produce uniform dispersion in the matrix. The homogeneous dispersion of fine reinforced particles in a fine grained matrix is beneficial to the mechanical properties of metal matrix composites [2]. A number of research works have been performed on processing of aluminum matrix composites via mechanical milling. Meanwhile, mechanical milling affects the morphology and hardness of powder particles, thus it influences the compressibility of milled powders [6].

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Materials are characterized by a grain size or particulate size of up to about 100 nm. These materials exhibit enhanced mechanical, magnetic, elevated temperature, optical, and excellent catalytic properties [7]. It was reported that the high-energy ball milling has been used to improve particle distribution throughout the matrix [8]. The microstructure analysis of Al–Al_2O_3 composite produced by mechanical alloying method was studied in [9]. In [10] the authors synthesized high volume fraction Al–Al_2O_3 nano composite powders by high-energy milling and studied the characteristics of the milled powders. X-ray diffraction is a convenient method for determining the mean size of crystallites in crystalline bulk materials. The first scientist, Paul Scherrer, published his results in a paper that included what became known as the Scherrer equation in 1981. This can be attributed to the fact that “crystallite size” is not synonymous with “particle size”, while X-Ray diffraction is sensitive to the crystallite size inside the particles.

The aim of present work is to prepare aluminium hybrid composite powders that consist of TiO_2 and Gr by using ball milling process. An attempt was made to calculate the grain size, lattice strain, stress, lattice space, lattice constant, dislocation density and unit cell volume of mechanically milled powders. The grain size was calculated by using Williamson-Hall and Scherrer equations. Microstructure analysis was carried out to reveal the presence of reinforcement particles during ball milling.

Experimental details. Atomized aluminium (Al) powder size of –325 mesh and purity of 99.7% supplied by Kemphasol, Mumbai, India was used for the matrix material and rutile phase of titanium-di-oxide (TiO_2) and graphite powders supplied by the Acechemie (India) were used as the reinforcement material. Natural Graphite is a mineral consisting of graphitic carbon. It varies considerably in crystallinity. Natural graphite is an excellent conductor of heat and electricity. It is stable over a wide range of temperatures. Graphite is a highly refractory material with a high melting point (3650°C). The required mass of Al, TiO_2 and Gr were accurately weighed in an electronic weighing machine. The powders were milled for 20 h in a ball mill with a speed of 100 r/min. The vial of the ball mill is made up of high hardened stainless steel material. Hardened high speed steel balls with a diameter of 10 mm were used and the ball-to-powder ratio was 1:1. X-ray diffraction analysis was carried out using PANalyticalX’Pert X-ray diffractometer CuK_α target, ($\lambda = 1.5418$ Å) to determine the lattice space, lattice constant, grain size, lattice strain, stress, dislocation density and unit cell volume of the milled composite powders by the following equations [11].

The grain size was calculated using Williamson-Hall equation:

$$\beta \cos\theta = \left(\frac{k\lambda}{t}\right) + \left(2\varepsilon \sin\theta\right), \tag{1}$$

where k is the shape factor (0.94); λ is the wavelength of the X-ray used ($\lambda = 1.5406$ Å); θ is the Bragg diffraction angle and β is the FWHM in radian; t is the effective crystallite size; ε is the strain value.

The Scherrer Equation is given by

$$D = \frac{0.94\lambda}{\beta \cos\theta}. \tag{2}$$

The strain value (ε) can be evaluated by using the following relation:

$$\varepsilon = \left(\frac{\lambda}{D \sin\theta}\right) - \left(\frac{\beta}{\tan\theta}\right), \tag{3}$$

where D is the grain size.

The dislocation density (δ) has been calculated by using the formula:

$$\delta = \frac{15\varepsilon}{aD}, \tag{4}$$

where ε is the strain value; a is the lattice parameter; D is the grain size.

The stress was calculated by using the formulae:

$$S = \frac{E}{2\delta}\left[\frac{a_0 - a}{a_0}\right] \tag{5}$$

The FWHM is calculated by the equation,

$$\beta = (2\theta\text{high} - 2\theta\text{low})X\left(\pi/180\right) \tag{6}$$

The lattice parameter was determined for each of the diffracting planes from XRD patterns.

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2},$$

where E is the Young's modulus of the powder; δ is the Poission's ratio of the powders; a_0 is the bulk lattice constant and a is lattice constant of the powders. In order to study the compressibility of the different powder blends, the density after compaction at pre-determined pressure was measured and recorded. The compressibility of powder mixtures were carried out using computerized universal testing machine of 400 kN capacity (Venus Instruments, India; Model: UTV-40PC, SR No.: 2011/[4084]) with suitable punch and die. The known values of relative densities and applied pressure have been used in the Heckel and Balshin compaction equation to validate the results. Standard deviation from the linearity of the measured values and regression equations for all samples were determined using Origin-8 software.

The milled Al + 5% TiO_2 + 6% Gr hybrid composite powders were compacted in 400 kN hydraulic press using punch and die. The compaction pressure was 500 MPa and the specimen dimensions were 24 mm diameter and 12 mm height. The sintering was done in a muffle furnace at the temperature of 590°C for a period of 3 h. The SEM analysis of the sintered Al + 5% TiO_2 + 6% Gr composite was conducted using FEI Quanta FEG 200-SEM. The microstructure analyses were carried out for the sintered hybrid composite specimen using an optical microscope and image analyzing software (Media Image Technologies Pvt. Ltd. Hyderabad) to study the grain boundary, bonding between the matrix and reinforcements.

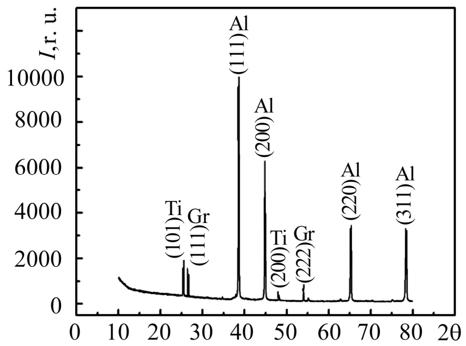

Fig. 1. XRD patterns of Al + 5% TiO_2 + 6% Gr composite powders.

Results and discussion. ***XRD analysis of milled powders.*** The XRD patterns of Al + 0% TiO_2, Al + 5% TiO_2, Al + 5% TiO_2 + 2% Gr and Al + 5% TiO_2 + 4% Gr composite powders, reported in previous publication are used to calculate the structural parameters [12]. In this study XRD pattern of Al + 5% TiO_2 + 6% Gr composite powders is provided in Fig. 1. The calculation of particle size, stress, unit cell volume, dislocation density, lattice constant and lattice strain of mechanically milled powders is very important since the phase constitution and transformation characteristics appear to be critically dependent on the above said properties. Average grain size, strain, stress and dislocation density are calculated using Eqs. (1)–(5) for all the composite powder blends and all the values are tabulated in Table. The cold working or plastic deformation of metal powders has been shown to produce appreciable changes in the intensity distribution of diffracted X-rays.

**Structural characteristic of Al + 0% TiO_2 (1), Al + 5% TiO_2 (2),
Al + 5% TiO_2 + 2% Gr (3), Al + 5% TiO_2 + 4% Gr (4)
and Al + 5% TiO_2 + 6% Gr (5) powders**

Lattice, Å		*D* (Scherrer), nm	ε, $\times10^{-3}$	*D* (WH), nm	Stress 10^{10}, dyne/cm^2	Dislocation density, lines/m^2	Unit cell volume 10^{-29}, Å
space	constant						
1.75	4.043	109.63±0.13	0.336	142.733±0.21	0.191	$1.182\cdot10^{14}$	6.607
3.05	5.919	168.07±0.11	0.672	178.471±0.14	1.857	$5.762\cdot10^{14}$	13.306
3.93	5.923	149.75±0.17	0.884	188.764±0.19	4.805	$3.316\cdot10^{18}$	13.342
3.45	4.967	136.56±0.08	0.672	174.843±0.23	5.483	$8.251\cdot10^{17}$	9.879
3.46	4.987	179.98±0.16	0.538	224.624±0.13	4.253	$1.504\cdot10^{17}$	9.999

Fig. 2 shows the effect of reinforcement addition on the grain size which is calculated by using Williamson-Hall and Scherrer Equations. It is observed from Fig. 2 that the increase in grain size has been observed for the addition of 5 weight percentage of TiO_2 to the Al matrix. The grain size increases with the addition of increasing weight percentage of graphite due to the agglomeration of the particles. The powder particle size is changing with milling time, as a result of the two opposing factors of cold welding and fracturing of powder particles. While cold welding increases the particle size, fracturing reduces the particle size. Hence, under continued milling with increasing weight percentage of graphite powders the particle size increases. It is expected that the addition of hard nature of TiO_2 powders will decrease the grain size. But here the increase in the grain size observed in the present study could be because of minimum milling time and energy. However the similar results were obtained in [14], the authors reported for the 2024 aluminum composites reinforced with various weight percentages of TiO_2 nanoparticles in the early stage of the milling, the A2024 powders are flattened by the collisions of ball–powder–ball. After this, TiO_2 particles are embedded into the A2024 powders and progressively dispersed in the matrix. Increased average particle size of the 12 h milled powder confirms that the A2024 powders undergo repeating plastic deformation, fracturing, and cold welding process [13]. The maximum stress strain values are obtained for the Al + 5% TiO_2 + 6% Gr composite powders. In [2] it was reported that when comparing with nano Al–TiO_2 composite the grain size of microcomposite is higher due to the more agglomeration of TiO_2 with aluminium matrix. Thus the agglomeration of reinforcement powders plays vital role during mecahnical milling process.

Compressibility of Al–TiO_2–Gr mixture powders. The experimental procedure of Al–TiO_2–Gr mixture powders compaction and the densification curves were presented in previous works [13]. In this study the Al+5%TiO_2+6%Gr powder mixture is compared with other composition of mixtures. The correlation between TiO_2 and Gr amount and relative density is shown in Fig. 3. It is noted that the maximum densification (98.4) was obtained for the unreinforced aluminium under the pressure of 500 MPa. However for the same compaction pressure the densification obtained for the Al + 5% TiO_2 + 6% Gr hybrid composites is 93.2%. The similar results were also reported in [14] for the Al–SiC composites. The authors of [15] explained that the reason for the decrease in densification could be that the ceramic reinforcement particles are harder than the base soft Al matrix powder and thus during compaction will not be extruded into the pore space.

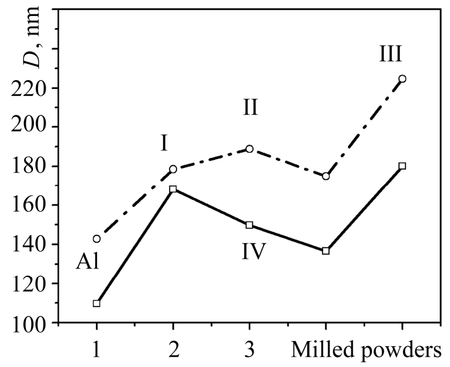

Fig. 2.

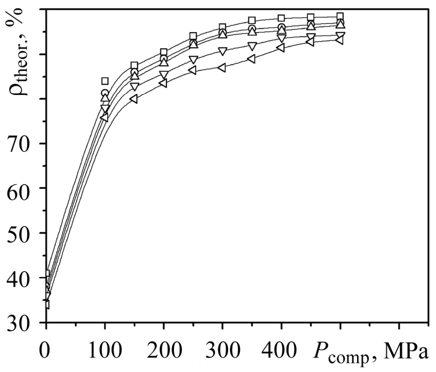

Fig. 3.

Fig. 2. Effect of reinforcements on the grain size. I – Al + 5% TiO_2; II – Al + 5% TiO_2 + 2% Gr; III – Al + 5% TiO_2 + 6% Gr; IV – Al + 5% TiO_2 + 4% Gr; □ – Scherrer equation; ○ – Williamson-Hall equation.

Fig. 3. Compressibility curves for milled powders. □ – Al; ○ – Al + 5% TiO_2; △ – Al + 5% TiO_2 + 2% Gr; ▽ – Al + 5% TiO_2 + 4% Gr; ◁ – Al + 5% TiO_2 + 6% Gr.

Experimental results using different compressibility equations. Al–TiO_2–Gr mixture powders were tested using the densification mathematical equation developed by the Heckel and Balshin. The first equation of Heckel taking into account processes occurring during pressing and this equation are applicable to metallic powders at 100…700 MPa, where substantial rearrangement of particles occurs. Figs. 4, 5 show the relationship between the relative density and applied pressure and regression equations for Al + 0% TiO_2, Al + 5% TiO_2, Al + 5% TiO_2 + 2% Gr, Al + 5% TiO_2 + 4% Gr and Al + 5% TiO_2 + 6% Gr samples. From the Balshin densification model, we understand that the encouragement of TiO_2 and Gr amount on the linearity of the model. It is observed that the deviation from the linearity of densification curves of experimental green compacts according in Heckel model is influenced by the presence of TiO_2 and Gr reinforcing elements. The similar results were obtained by the authors in [14] who reported for the aluminium based composites reinforced with silicon carbide particles during compaction.

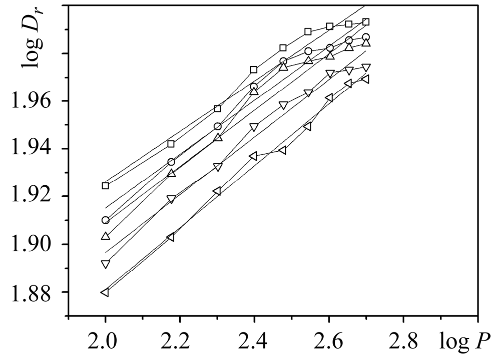

Fig. 4.

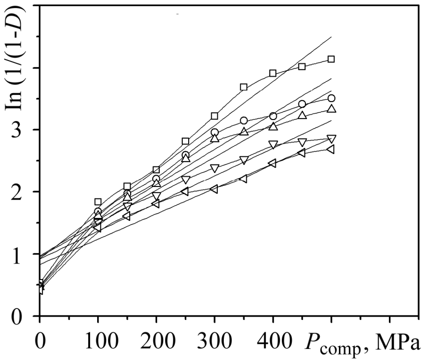

Fig. 5.

Fig. 4. Densification curves according to Balshin equation. (1) = $0.1058x + 1.7145$: $R^2 = 0.96385$; (2) = $0.1131x + 1.6889$: $R^2 = 0.9586$; (3) = $0.1183x + 1.6723$: $R^2 = 0.96536$; (4) = $0.1298x + 1.6214$: $R^2 = 0.99138$; (5) = $0.1208x + 1.6547$: $R^2 = 0.9787$ (designations as in Fig. 3).

Fig. 5. Densification curves according to Heckel equation. $y = 0.00714x + 0.9249$: $R^2 = 0.9571$; $y = 0.00573x + 0.9692$: $R^2 = 0.9237$; $y = 0.00535x + 0.9552$: $R^2 = 0.9127$; $y = 0.0.00446x + 0.9225$: $R^2 = 0.9001$; $y = 0.00406x + 0.8338$: $R^2 = 0.9127$ (designations as in Fig. 3).

Microstructural analysis of sintered composite. The cross section of the sintered sample was prepared to reveal the uniform distribution of hard particles in aluminium matrix. Fig. 6*a* shows the scanning electron microscope image of the sintered Al + 5% TiO_2 + 6% Gr hybrid composite. It showed reasonably uniform distribution of reinforcement particles and good interfacial integrity. The uniform distribution of hard TiO_2 and Gr reinforcement particles was achieved because of ball milling process with suitable ball milling parameters. The size of the reinforcement particles also measured by SEM instrument and displayed in Fig. 6*b* in nanometers. Fig. 7 shows the cross sectional microstructure image of Al + 5% TiO_2 + 6% Gr hybrid composite obtained from optical microscope. Generally, the reinforcement particles were clearly identified in the cross sectional image [16]. Here TiO_2 and Gr reinforcement particles are well distributed in aluminium matrix and they are seen as black and gray color.

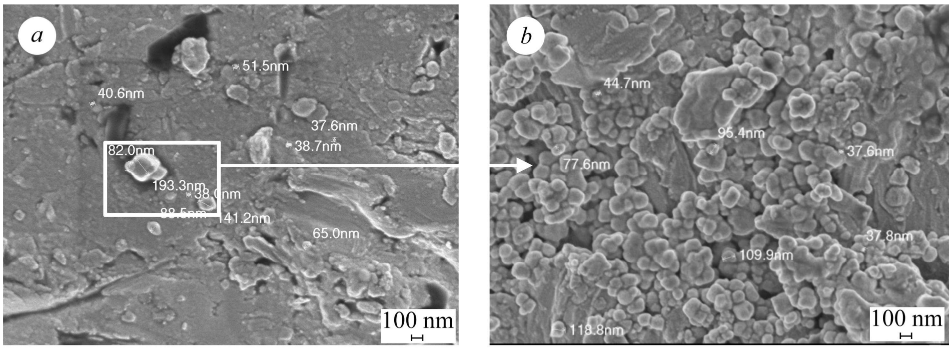

Fig. 6. SEM image of sintered (*a*) Al + 5% TiO_2 + 6% Gr hybrid composite (*b*), magnified view of (*a*) shows the size of TiO_2 particles.

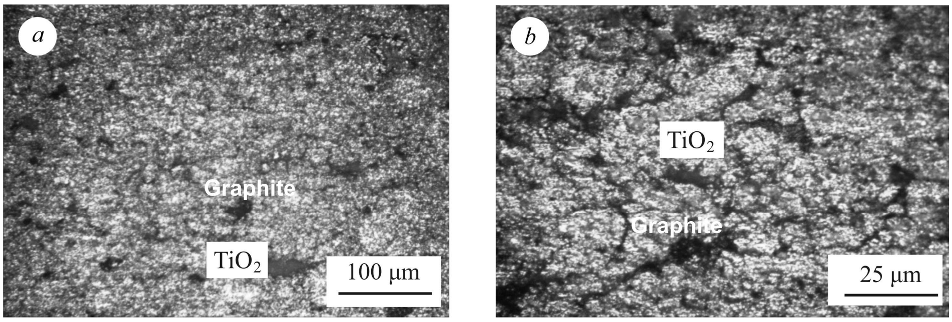

Fig. 7. Optical microscope image of sintered Al + 5% TiO_2 + 6% Gr hybrid composite: *a* – 100 μm scale; *b* – 25 μm scale.

CONCLUSIONS

Aluminium hybrid composite powders have been successfully synthesized after 20 h of ball milling at the speed of 100 rpm. The grain size of the milled powders was calculated by using Williamson Hall equation. For Al + 5% TiO_2 + 6% Gr hybrid composites the grain size was achieved as 224.624 nm and for the unreinforced aluminium the grain size was 142.733 nm. The increase in grain size is due to the cold welding and agglomeration of both hard and soft reinforcements with the ductile nature of matrix materials. The lattice constant, lattice space, dislocation density, unit cell volume, stress, and strain for all the milled composite powders were established. Adding the hard and brittle TiO_2 and soft Gr powders in the soft aluminium the compressibility decreases, this decreasing is in agreement with the experimental compressibility curves and the calculated (according to Heckel and Balshin model) compressibility curve, for

all mixtures. It is noted that the maximum densification (98.4) was obtained for the unreinforced aluminium at a pressure of 500 MPa. However for the same compaction pressure the densification obtained for the Al + 5% TiO_2 + 6% Gr hybrid composites is 93.2%. Scanning electron microscope analysis ensures that the uniform distribution of reinforcement (TiO_2 and Gr) particles in the Al matrix and the sizes were displayed in the SEM images. Optical microscopic analysis reveals the formation of grain boundary and the interfacial bonding between the reinforcements and the matrix.

РЕЗЮМЕ. Вивчали характеристики композитних порошків Al + TiO_2 + Gr. Композити складу Al + 0% TiO_2, Al + 5% TiO_2, Al + 5% TiO_2 + 2% Gr, Al + 5% TiO_2 + 4% Gr та Al + 5% TiO_2 + 6% Gr отримували шляхом кульового помелу відповідних компонентів. Для визначення розмірів зерен, параметрів кристалічної решітки, напруження, деформації, густини дислокацій та об'єму елементарної комірки використовували рентгенівський дифракційний аналіз. Здатність до компактування Al з сумішшю порошків 5 wt.% TiO_2 та 2 і 4 wt.% Gr визначали в гартованих сталевих прес-формах за тиску 100… 500 MPa. Для розуміння особливостей компактування гібридних композитів на основі Al, зміцнених частинками TiO_2 та Gr за різних тисків, виконували експериментальні дослідження з використанням декількох підходів. Наведено мікроструктурний аналіз композита Al + 5% TiO_2 + 6% Gr.

РЕЗЮМЕ. Изучали характеристики композитных порошков Al + TiO_2 + Gr. Композиты состава Al + 0% TiO_2, Al + 5% TiO_2, Al + 5% TiO_2 + 2% Gr, Al + 5% TiO_2 + + 4% Gr и Al + 5% TiO_2 + 6% Gr получали путем шарового помола соответствующих компонентов. Для определения размеров зерен, параметров кристаллической решетки, напряжения, деформации, плотности дислокаций и объема элементарной ячейки использовали рентгеновский дифракционный анализ. Способность к компактированию Al со смесью порошков 5 wt.% TiO_2 и 2…4 wt.% Gr определяли в закаливаемых стальных пресс-формах при давлении 100...500 MPa. Для понимания особенностей компактирования гибридных композитов на основе Al, упрочненных частицами TiO_2 та Gr при различных давлениях, проводили экспериментальные исследования с использованием нескольких подходов. Представлен микроструктурный анализ композита Al + 5% TiO_2 + 6% Gr.

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