Experimental Characterization of Aluminum-Based Hybrid Composites Obtained Through Powder Metallurgy

D F Marcu¹, M Buzatu¹, V G Ghica¹, M I Petrescu¹, G Popescu¹, F Niculescu¹ and G Iacob¹,*
¹ Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, 313 Splaiul Independentei Blvd, 060042, Bucharest, Romania
E-mail: iacob_gh@yahoo.com

Abstract. The paper presents some experimental results concerning fabrication through powder metallurgy (P/M) of aluminum-based hybrid composites - Al/Al₂O₃/Gr. In order to understand the mechanisms that occur during the P/M processes of obtaining Al/Al₂O₃/Gr composite, we correlated the physical characteristics with their micro-structural characteristics. The characterization was performed using analysis techniques specific for P/M process, SEM-EDS and XRD analyses. Micro-structural characterization of the composites has revealed fairly uniform distribution this resulting in good properties of the final composite material.

1. Introduction

There are numerous researches [1-8] to obtain metal matrix composites and one type of hardening material (ceramic particles of Al₂O₃, SiC, Gr, TiC, B₄C, etc.). Regarding hybrid composite materials, the international literature contains a series of data to demonstrate the scientific applicability of composites with aluminum metallic matrix hardened with SiC, Al₂O₃ and nickel-coated graphite Al/ SiC + Al₂O₃, Al/ SiC + Gr, Al/Al₂O₃ + Gr or Al/ SiC + Gr-Ni. The major advantage of hybrid composites lies in the possibility of modulating the properties and thus obtaining a wide range of materials, the use of which can be extended to almost all areas of technical activity [5, 7, 9, 10].

Aluminum matrix hybrid composites hardened with ceramic particles (Al₂O₃, SiC, Gr) have much better mechanical properties than unalloyed aluminum alloys and have for some time been used as tribological parts due to their high strength/density ratio, showing a significant improvement in tribological properties, including wear resistance, abrasion resistance and galling resistance [7, 9-14].

By varying the nature of the components and their volume fraction, the properties of the hybrid composites can be adjusted. Increasing the content of the hardening element generally leads to an appreciable increase in the durability of semi-finished products. Any of the matrix composite production techniques involves, in a first step, mixing the components (the metal matrix and the hardening particles) so as to obtain a uniform distribution of the material, a high resistance interface and a controlled microstructure, and in a second stage the forming of the mixed material by various technologies (casting, powder metallurgy, plastic deformation etc) [15-18].

Solid state techniques have several advantages, such as a low processing temperature, which results in a low interaction of matrix-hardener and therefore good mechanical properties can be obtained. Solidification defects (shrinkage, porosity, segregation) are avoided and, in general, a more uniform distribution of the hardener can be obtained. The most common technique in solid state is powder metallurgy. Powder metallurgy is an important branch of modern technology, the emergence of this
technique being determined by the necessity of obtaining materials with special characteristics that can not be achieved by classical processes. It should be noted that at present, the automotive industry, the household appliance industry, electrical measuring and control instruments, sports equipment, television sets and even rockets can not be designed without the use of powder metallurgy [19-21].

One of the successful methods applied to obtain uniform and homogeneous powders is the method of mechanical alloying. This is a solid state processing technique that allows the synthesis of new alloys that cannot be obtained by any other technique. Mechanical alloying is a process of grinding with high velocities and kinetic energies that can be carried out in a dry or wet environment, and is used to manufacture a variety of advanced materials and alloys (over-saturated solid solutions, amorphous materials, intermetallic compounds and MMCs). Mechanical alloying is a simple and useful technique for achieving a homogeneous distribution of inert fine particles in a fine grain matrix [20-22]. The main purpose of this paper was to obtain hybrid composites with aluminum metal matrix using mechanical alloying followed by compaction and sintering processes. Alumina was chosen as hardening material and graphite was chosen to improve the tribological properties. The characterization of samples was performed using analysis techniques specific for P/M process, SEM-EDS and XRD analyses.

2. Materials and methods

Powders of aluminum, alumina, graphite and zinc stearate were homogenized and mechanically alloyed in a RETSCH PM 400 high energy planetary mill. The experiments were carried out in a dry environment using zinc stearate as a process control agent to avoid powder agglomeration as well as depositing it on the walls of the vials and on the balls used for milling. The speed of the mill was kept constant, with a rotational speed of 300 rpm. The grinding time was 4 hours. The size of the elemental powders from which the mechanical alloying process is started is of the order of the microns, the powders having a fairly high purity, as can be seen from Tables 1-4, following the grinding process resulted a very small granulations, as will be demonstrated (even the nanometric order), which ensures a uniform and homogeneous structure of the hybrid composites.

The compositions selected to investigate the effects of the amount of hardening elements in the Al/Al₂O₃/Gr hybrid composites are shown in Table 1.

| Notation | Al (wt. %) | Al₂O₃ (wt. %) | Graphite (wt. %) |
|----------|------------|---------------|-----------------|
| HyCo 1   | 89         | 10            | 1               |
| HyCo 2   | 84         | 15            | 1               |
| HyCo 3   | 79         | 20            | 1               |
| HyCo 4   | 87         | 10            | 3               |
| HyCo 5   | 82         | 15            | 3               |
| HyCo 6   | 77         | 20            | 3               |

The mechanical alloying process started from raw materials in the form of powders of micron size and with high purity (Al - 44 μm and 99.5%, Al₂O₃ - 44-150 μm and 98.5%, Gr < 32 μm and 95%), their average size decreasing by almost half. The zinc stearate powder was 1% of the total mass of the powder. For the production of Al/Al₂O₃/Gr hybrid composites the Al powder was used as a ductile matrix, Al₂O₃ powder was used as a hardener and the graphite powder as lubricant. The chemical compositions and specifications of powders according to the supplier's technical sheet are shown in Table 2 to 5.
Table 2. Chemical composition of aluminum powder (Al).

| Element | wt.% |
|---------|------|
| Fe      | 0.11 |
| Si      | 0.04 |
| Cu      | 0.01 |
| Mn      | < 0.01 |
| Cr      | < 0.01 |
| Ni      | < 0.01 |
| Zn      | < 0.01 |
| Ti      | < 0.02 |
| Ga      | < 0.01 |
| Fe      | 0.11 |

Table 3. Chemical composition of alumina powder (Al₂O₃).

| Element   | wt.% |
|-----------|------|
| SiO₂      | max. 0.015 |
| Fe₂O₃     | max. 0.020 |
| Na₂O      | max. 0.450 |
| CaO       | max. 0.050 |
| P₂O₅      | max. 0.0012 |
| K₂O       | max. 0.018 |
| Li₂O      | max. 0.017 |
| ZnO       | max. 0.0015 |
| V₂O₅      | max. 0.0025 |
| TiO₂      | max. 0.0025 |

Table 4. Chemical composition of graphite powder (Al).

| Component | wt.% |
|-----------|------|
| C         | 95   |
| Fe        | max. 0.5 |
| S         | max. 0.1 |
| Ash       | max. 2 |

Table 5. The specifications of the raw material for the zinc stearate.

| Component          | wt.%          |
|--------------------|---------------|
| Zn content         | 10.3 – 11.3   |
| Fat acids          | max. 0.5      |
| Humidity           | max. 0.8      |
| Density            | 1.095         |
| Melting temperature| 120 – 130     |

Secondary electron image analysis (SEI) was performed at a resolution of up to 2.98 μm, in a magnification range up to 100,000X, at a 30 kV acceleration voltage in high vacuum, with the use of the scanning electron microscope Quanta Inspect F50, with a field emission gun (FEG) with 1.2 nm resolution and an Energy Dispersive X-ray Spectrometer (EDXS). XRD data were obtained using a Panalytical X’PERT MPD X-ray diffractometer with a Cu Kα radiation source (λ = 1.5418 Å) in the range of 2θ = 10–90°.

The hardness of compressed samples from composite powders obtained by mechanical alloying and subsequently sintered was determined by the Leeb Rebound Hardness Test (LRHT), using the NAMIKON hardness tester.

3. Results and discussions

3.1. Technological properties of the Al/Al₂O₃/Gr hybrid composites

For the samples obtained after pressing (Atlas™ 15T Manual Hydraulic Press from SPECAC) and sintering processes (was realized in a heating induction furnace, Balzers type, sintering temperature: 620°C; 60 minute exposure time) the technological characteristics (density, compactness, porosity, etc.) were determined. The physic-technological properties determined on the hybrid composites samples with different compositions, determined according to the specific powder metallurgy procedures, and are shown in Figures 1 to 3, the notation of the samples being presented in Table 1.

The densities of the hybrid composites after sintering show a significant increase compared to the densities after pressing. As can be seen from Figure 1, densities after sintering show a decreasing trend with increasing the Al₂O₃ content from 10 wt. % to 20 wt.% and maintaining a constant content of 1
wt. % Gr, and an oscillating tendency with increasing the Al₂O₃ content from 10 wt.% to 20 wt.% and maintaining a constant content of 3 wt.% Gr.

![Figure 1](image1.png)

**Figure 1.** Density of the Al/Al₂O₃/Gr hybrid composites.

![Figure 2](image2.png)

**Figure 2.** Compactness and porosity after pressing the Al/Al₂O₃/Gr hybrid composites.

The compactness of the Al/Al₂O₃/Gr after pressing process shows a decreasing trend with the increase of Al₂O₃ content. Regarding the variation of the values according to the graphite content we can note a slight decrease, except for HyCo 5. The maximum value corresponds to HyCo 1 and the minimum value corresponds to HyCo 4, both having a 10% Al₂O₃ content but differing graphite content. The porosity values of the tablets are complementary to the compactness values.

After the sintering process of the Al/Al₂O₃/Gr tablets we can observe an improvement in values. Similar to the data presented above they shows a decreasing trend with the increase of Al₂O₃ content. Regarding the variation of the values according to the graphite content we can note a slight decrease, except for HyCo 6. The maximum value corresponds to HyCo 1 and the minimum value corresponds to HyCo 3. The porosity values of the tablets are complementary to the compactness values.

The degree of porosity of the samples is calculated according to the initial density of the tablets and increases with the increase of the reinforcement content of the hybrid composites. From the data presented above, it is observed that the degree of porosity after sintering of the samples is much lower than that of the pressed tablets. This reduction is due to the elimination of voids between the particles and the contraction after sintering.
3.2. Micro-structural investigations

These analyzes were performed in order to observe the formation, appearance and diameter of the grains, as well as particle identification at very high magnifications. At the same time, it was possible to determine precisely the distribution of the constituent elements of the examined samples. For this purpose we chose sample 6 with maximum content of Al$_2$O$_3$ (20 wt. %) and graphite (3 wt. %). The micro-structural aspect of the analyzed sample is shown in Figures 4 and 5.

The distribution of the main elements in the composition of the analyzed sample is presented in the images associated with the chemical analysis. The images highlight the C (red), O (yellow) and Al (blue) content of HyCo 6 powder composition after 4 hours of mechanical alloying, obtained by analyzing the hue differences in the images. It can also be seen in the micro-analyzed area the presence of a particle of Gr on which grains of Al$_2$O$_3$ are trapped.
The presence of only the Al, C and O elements indicated by the spectrum of analysis, and the fact that no other elements are indicated, confirms that the powders are not contaminated with other elements that may come from other sources.

Also by means of electronic microscopy, the size of microcrystalline and even nanocrystalline compounds formed between the Al and Al₂O₃ and Gr powders shown in Figure 5 was determined. Determination of the grain size in the analyzed samples was very difficult to determine due to the very fine particle agglomeration. It is recommended that particle-dispersing equipment be used before analyzes are performed. The grain size was approximately between 295.0 nm and 1.63 μm.

![Image of SEM-ETD image of the HyCo 6.](image)

**Figure 5.** SEM-ETD image of the HyCo 6.

The diffraction patterns of the hybrid composites after 4 hours of mechanical alloying exhibit various peaks corresponding to the face centered cubic phase of Al. The α-Al₂O₃, β-Al₂O₃, and δ-Al₂O₃ phases were observed in the diffraction patterns (Figure 6), these being phases with great stability.

![Image of XRD analysis of the HyCo 6.](image)

**Figure 6.** XRD analysis of the HyCo 6.

Through micro-structural analyzes it was observed at very large scale, provided by SEM microscopy, forming a very fine sub-grain structure with diameters of hundreds of nanometers, beneficial for mechanical stress behavior.
3.3. Hardness testing

Determination of the hardness of hybrid composites after pressing and sintering was done by the Leeb method to illustrate the effect of alumina (10, 15 and 20 wt. %) and graphite (1 and 3 wt. %). Figure 7 presents the results from the determination of the samples belonging to the HyCo 1-6 group, which have been studied in this paper.

![Figure 7. Comparison between hardness results on tablets and after sintering.](image)

Figure 7. Comparison between hardness results on tablets and after sintering.

Leeb hardness of hybrid composite tablets pressed or sintered shows an increasing trend by rising the content of Al₂O₃ and Gr, there is also a significant increase in values of sintered tablets compared to pressed tablets, as demonstrated by the analysis of the test results by other methods of determining the hardness [13].

4. Conclusions

Following the experimental process of mechanical alloying, various compositions of Al/Al₂O₃/Gr composite powders were produced, which were pressed and subsequently sintered, thus completing a complete powder metallurgy cycle.

The physico-technological, microstructural and mechanical properties were investigated demonstrating promising results. The result obtained from present work can be summarized in the following points:

- Densities of the HyCo 1-6 samples after sintering show a significant increase compared to the densities after pressing; these can be greatly improved if higher compaction pressures are used.
- The results of the compactness and porosity of the HyCo 1-6 samples shows an improvement after sintering process of the Al/Al₂O₃/Gr tablets we can observe an improvement in values.
- The porosity values of the tablets are complementary to the compactness values. They are calculated according to the initial density of the tablets.
- The composition of the analyzed sample indicates only the presence of Al, C and O elements, which means there is no contamination of the powders.
- According to the SEM analysis the grain size in the investigated micro-zone was approximately between 295.0 nm and 1.63 μm, meaning that was formed a fine and homogeneous structure.
- The hardness results of of HyCo 1-6 samples tablets and shows an increasing trend with the content of Al₂O₃ from the 10 wt. % to 20 wt. % and Gr from 1 wt. % to 3 wt. %, there is also a significant increase in values of sintered tablets compared to pressed tablets.
5. References

[1] Mendoza-Duarte J M, Estrada-Guel I, Carreño-Gallardo C and Martínez-Sánchez R 2015 *Journal of Alloys and Compounds* **643** S172-S177

[2] Tousi S S R, Rad R Y, Salahi E, Rahimipour M R, Kazemzade A and Razavi M 2009 *International Journal of Engineering. Transactions B: Applications* **22** 169-178

[3] Ibrahim I A, Mohamed F A, Lavernia E J 1991 *Journal of Materials Science* **26** 1137-1156

[4] Singla M, Dwivedi D D, Singh L, Chawla V 2009 *Journal of Minerals & Materials Characterization & Engineering* **8** 455-467

[5] Włodarczyk-Fligier A, Dobrzański L A, Kremzer M, Adamiak M 2008 *Journal of Achievements in Materials and Manufacturing Engineering* **27** 99-102

[6] Kok M 2005 *Journal of Materials Processing Technology* **161** 381-387

[7] Güler O, Çuvalci H, Gökdağ M, Çanakçı A, Çelebi M 2017 *Particulate Science and Technology*, http://dx.doi.org/10.1080/02726351.2017.1326994

[8] Yin S, Xie Y, Cizek J, Ekoı, Hussain T, Dowling D, Lupoi R 2017 *Composites Part B* **113** 44-54

[9] Ekka K K, Chauhan S R, Goel V 2015 *Proceedings of the Institution of Mechanical Engineers, Part L: Journal of Materials Design and Applications* **230** 537-549

[10] Moghadam A D, Omrani E, Menezes P L, Rohatgi P K 2015 *Composites Part B: Engineering* **77** 402–420

[11] Han Q, Geng Y, Setchi R, Lançan F, Gu D, Evans S L 2017 *Composites Part B* **127** 26-35

[12] Ahmad Z, Khan S 2014 *International Journal of Current Engineering and Scientific Research (IJCESR)* **1** 1-8

[13] Iacob G, Ghica V G, Buzatu M, Buzatu T, Petrescu I M 2015 *Composites: Part B* **69** 603–611

[14] Zabihi M, Toroghinejad M R, Shafyei A 2016 *Materials Science and Engineering: A* **667** 383-390

[15] Gürbüz M, Şenel M C, Koç E 2018 *Journal of Composite Materials* **52** 553-563

[16] Chen S H, Wang T C 2002 *Acta Mechanica* **157** 113-127

[17] Ramesh B, Senthivelan T 2010 *IACSIT International Journal of Engineering and Technology* **2** 1-6

[18] Kittali P, Satheesh J, Anil Kumar G, Madhusudhan 2016 *International Research Journal of Engineering and Technology (IRJET)* **03** 2412-2416

[19] Whittaker D 2008 *European Powder Metallurgy Association* 1-31

[20] Suryanarayana C 2001 *Progress in Materials Science* **46** 1-184

[21] El Eskandarany M S 2001 *William Anderson Publishing* New York USA

[22] Iacob G., Popescu G., Miculescu F., Buzatu M 2012 *U.P.B. Sci. Bull., Series B* **74** 221-230

Acknowledgments
This work has been supported by a grant of the University Politehnica of Bucharest, Program for research - Excellence Research Grants – GEX, project number 27/2017.

We hereby acknowledge the research founds project UPB-GEX 2017 (internal no. SM 35-17-04, ctr. No 70/2017) for providing the infrastructure used in this work and the project.