

MICROSTRUCTURE CHARACTERIZATION OF SiC REINFORCED ALUMINIUM AND Al4Cu ALLOY MATRIX COMPOSITES

A conventional powder metallurgy method (PM) was used to produce Al-SiC and Al4Cu alloy matrix composites with 2.5, 5, 7.5 and 10 wt% of SiC particles. Two different sizes of the reinforcing phase particles were applied to determine their effect on composite microstructure. The sintering process was carried out at 600°C under nitrogen atmosphere, and its consequence was the appearance of aluminium nitrides in composite microstructure acting as an additional strengthening phase. The composites were next re-pressed and re-sintered (2p2s) under the same conditions. The main aim of this article was to examine the microstructure of the SiC reinforced Al and Al4Cu alloy matrix composites. To achieve this goal and characterize the sintered materials, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques were used.

Keywords: metal matrix composites, aluminium, SiC, sintering atmosphere, microstructure

1. Introduction

Owing to their properties, aluminium and its alloys find a wide range of applications. What mainly accounts for this fact is the possibility of reducing the weight of vehicles and thus increasing the fuel efficiency with less pollution emitted to the atmosphere [1]. To increase the poor mechanical and tribological properties of aluminium and its alloys at elevated temperatures, their excessively soft matrix is reinforced with hard particles of oxides and carbides [2]. The addition of silicon carbide particles significantly improves the strength and hardness of aluminium and its alloys. The volume fraction of the reinforcement is less than 30% in the composites used for structural and wear resistant applications, but it can reach almost 70% in electronic packaging applications [3]. A significant effect on the obtained mechanical properties has the amount and size of the introduced reinforcement particles, since it is the size of the particles that determines the strengthening mechanism. Properly distributed particles not only hinder the movement of dislocations causing an increase in the mechanical properties but also prevent the grain growth process in the composite matrix and enhance the wear resistance.

The authors of [4] observed improved wear resistance and hardness of aluminium composites as a result of the introduction of higher content of SiC particles (from 4 vol% to 10 vol%). However, in [5], the authors reported a decrease of hardness after exceeding the 20% content of SiC particles. In [6], the

authors noticed that hardness of Al-SiC composites could be raised also with the addition of copper. Even more interesting was the fact that the weight loss investigated in tribological tests was lower for alloys containing copper. Aluminium-copper matrix composites were subjected to precipitation hardening to obtain higher mechanical properties. The authors of [7], after the heat treatment process of Al-5 wt% Cu composites obtained the growth of hardness from 70 to 107 HB.

The best known methods for the fabrication of Metal Matrix Composites (MMCs) are casting techniques and powder metallurgy (PM) [6], the latter one comprising the following steps: blending, compacting in dies and sintering. Limitations of the PM process include the size and weight of the final product. Nevertheless, with the application of PM it is possible to produce economically viable complex parts of a near net shape [5]. Regardless of the method chosen for the Al matrix composites manufacture, the most important in microstructure modelling is obtaining a homogenous distribution of reinforcement in the composite matrix, providing isotropic mechanical properties and uniform stress distribution in the sintered product without an adverse effect on the mechanical and electrical properties of Al-SiC composite materials. Homogeneous distribution of particles in the matrix of the composites made by PM is possible through appropriate selection of the size of powder particles of both matrix and reinforcing phase, combined with the application of correct process parameters as early as at the stage of blending [1,3,7,8].

* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF NON FERROUS METALS, DEPARTMENT OF MATERIALS SCIENCE AND NON-FERROUS METALS ENGINEERING, AL. MICKIEWICZA 30, 30-059 KRAKÓW, POLAND

** AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF METALS ENGINEERING AND INDUSTRIAL COMPUTER SCIENCE, DEPARTMENT OF PHYSICAL AND POWDER METALLURGY, AL. MICKIEWICZA 30, 30-059 KRAKÓW, POLAND

[#] Corresponding author: bleszcz@agh.edu.pl

In this study, Al and Al-4 wt% Cu alloys with the addition of silicon carbide particles were fabricated using conventional PM techniques. The aim of the article was to examine and characterize the microstructure of SiC reinforced aluminium and Al4Cu alloy matrix composites applying different particle size of the reinforcing phase fabricated by sintering under nitrogen atmosphere at 600°C.

2. Experimental procedure

The fabricated test composites were based on aluminium and Al-4 wt% Cu alloy with various amounts of silicon carbide as a reinforcement. The aluminium powder particles produced by argon gas atomization had an average size of $<63 \mu\text{m}$, the size of electrolytic copper powder was below $63 \mu\text{m}$. The SiC reinforcement was used in the form of particulate and was added to the alloy matrix in quantities equal to 2.5, 5, 7.5 and 10 wt%. To study the effect of particle size on composite microstructure, two different SiC powders were used: a coarse fraction with particle size ranging from 40 to $60 \mu\text{m}$ and a fine fraction with particle size of less than $2 \mu\text{m}$ (Fig. 1).

Pure aluminium powders and copper-alloyed aluminium powders were mixed with SiC reinforcement for 30 minutes in

a Turbula T2F mixer to produce a homogenous mixture. The mixed powders were pressed at room temperature under a pressure of 300 MPa in a rigid die on a single-action compaction press. The die wall was lubricated with glycerine to reduce the powder-wall friction and allow pulling out the green compact from the die orifice after the compacting had been completed.

The green compacts were sintered under nitrogen atmosphere at 600°C for 60 minutes. The basic purpose of sintering was to provide sufficient diffusion bonding between particles indicating the required degree of densification of the composite material. Additionally, to improve the density and mechanical properties of the obtained materials, the double pressing and double sintering operations (2p2s) were conducted under the same conditions.

To examine the microstructure of aluminium and Al4Cu alloy matrix composites and the distribution of ceramic particles therein, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used. Information about the chemical composition and phase composition of samples was provided by the EDS and X-ray diffraction (XRD) analyses. The bulk densities of the composites after sintering were measured by geometric method. Additionally, to check the relationship between microstructure and mechanical properties, the Brinell hardness values were determined for all the composites using a 2.5 mm diameter carbide ball and the applied force of 62.5 kG.

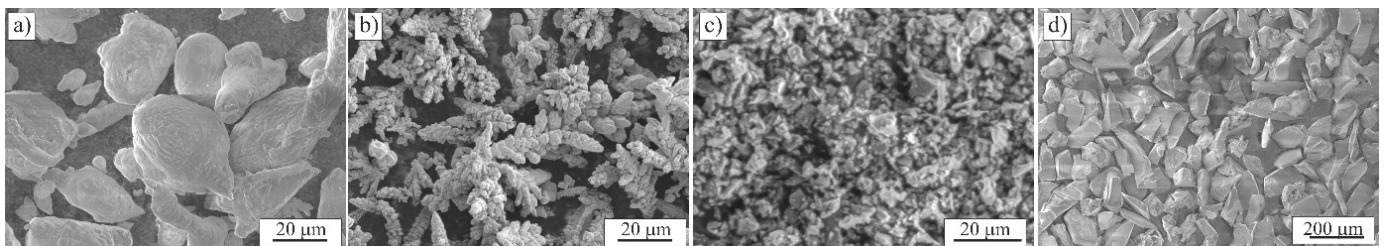


Fig.1. SEM micrographs of powders; a-aluminium, b-copper, c, d-SiC; SEM

3. Results and discussions

3.1. Density Evolution

The graphs presented in Figures 2 and 3 illustrate the effect of double pressing and double sintering on the relative density of aluminium and Al4Cu alloy matrix composites with SiC particles of different sizes related to the weight fraction of these particles. The addition of hard silicon carbide phase resulted in the decrease of relative density of both aluminium and aluminium alloy based composites. The application of large reinforcement particles, i.e. of the size between 40 and $60 \mu\text{m}$, allowed obtaining higher levels of densification compared to the composites reinforced with SiC particles of the size of less than $2 \mu\text{m}$. The increase in relative density was accompanied by the decrease in porosity. The highest value of density was obtained in samples without the addition of silicon carbide and with the Al4Cu matrix, the relative density of which has reached almost 95%. In all samples, compared to the first sintering operation, the additional press-

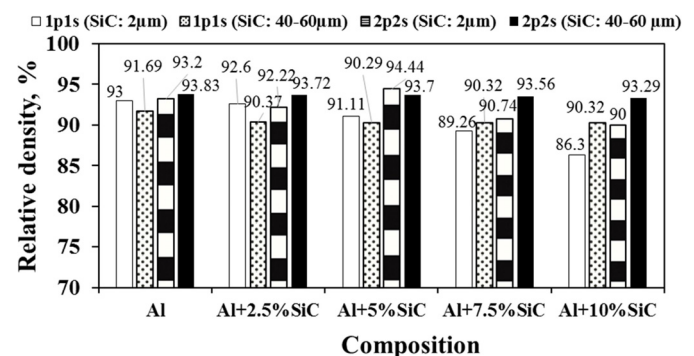


Fig. 2. Relative densities of as-sintered PM Al matrix composites depending on process parameters

ing and sintering enhanced even more the relative density and hardness, mainly through stronger bonds produced between the composite particles. As shown by microstructure examinations, the real porosity was smaller than the porosity determined by geometrical method; pores were observed only occasionally.

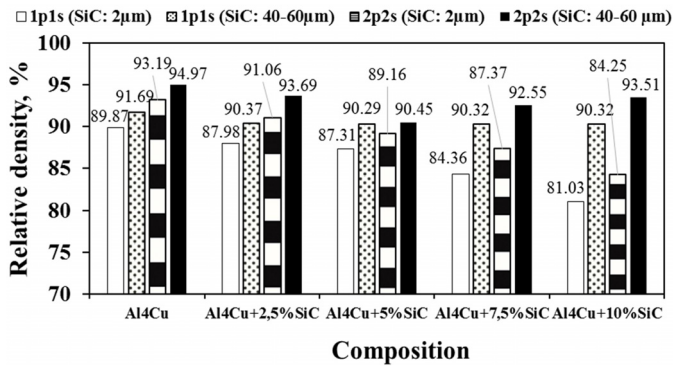


Fig. 3. Relative densities of as-sintered PM Al4Cu alloy matrix composites depending on process parameters

3.2. Microstructural investigations

Microstructure of as-sintered PM aluminium and Al4Cu alloy is presented in Figure 4. Regular shape of aluminium grains and scarce pores are observed; in Al4Cu alloy, some precipitates additionally appear on grain boundaries.

The results of chemical analysis carried out in micro-regions of the aluminium matrix presented in Figure 5 show Al₂O₃ oxides

present on grain boundaries (points 1,2,3). Due to the strong affinity for oxygen, aluminium particles are covered with a thin oxide layer which acts as a barrier to the interfacial bonding of particles and may affect the final properties of composites [7]. On the other hand, the presence of Al₂O₃ film with the fine-dispersed particles of Al₂O₃ has also a positive effect acting as an additional strengthening phase. During compaction, the oxide coating on the surface of the aluminium powder particles can break, which improves the interfacial bonding strength and enhances the adhesion between particles [9,10].

The layer of Al₂O₃ oxide covering the Al powder particles is usually amorphous and thermodynamically unstable, and as such may easily undergo transformation into a crystalline form during sintering. This is mainly due to its thickness exceeding the critical value of the thickness of an amorphous film through further oxidation resulting in the loss of stability and temperature rise above approximately 400°C which can initiate structural changes. As a result of the transformation of amorphous Al₂O₃ into crystalline γ -Al₂O₃, on account of differences in the densities of these two products, the integrity of the continuous oxide layer is broken and active aluminium metal surface is unveiled allowing for direct contact between aluminium and the atmosphere [1]. Breaking of the oxide layer during heating is also due

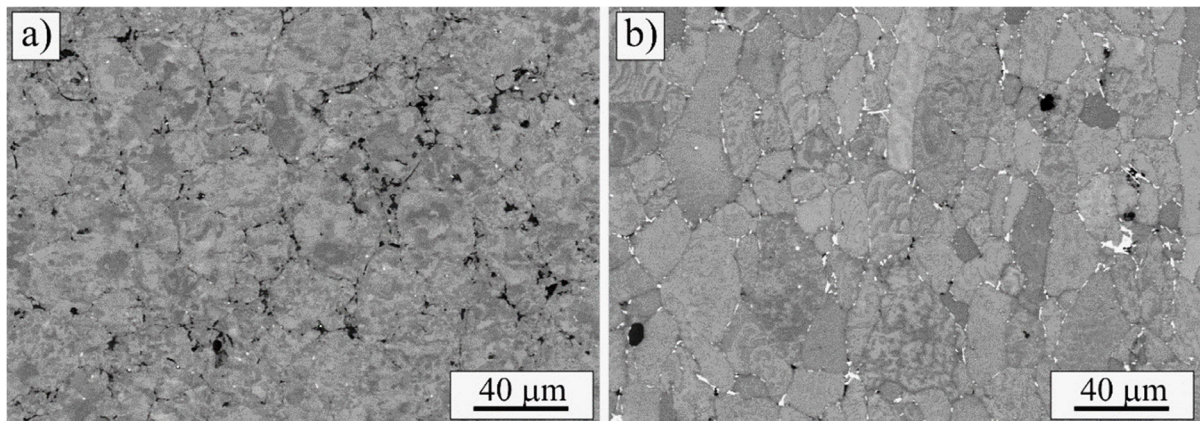
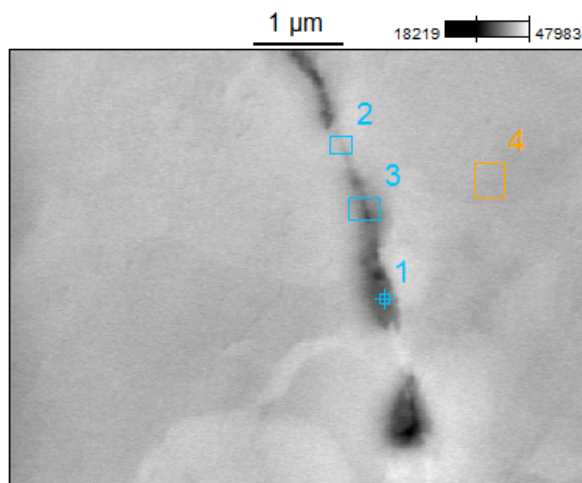


Fig. 4. Microstructure of PM: a) aluminium, b) Al4Cu alloy; SEM

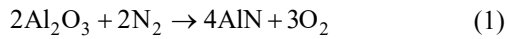


% weight		
No	O-K	Al-K
1	5.63	94.37
2	2.58	97.42
3	3.09	96.91
4	0.55	99.45
% atomic		
No	O-K	Al-K
1	9.14	90.86
2	4.27	95.73
3	5.10	94.90
4	0.92	99.08

Fig. 5. Chemical analysis carried out in micro-regions of as-sintered (2p2s, 600°C) pure Al matrix, SEM

to the presence of stresses generated by a large difference in the thermal expansion coefficients, which assume much higher values for aluminium than for the γ - Al_2O_3 [1,11].

Aluminium oxides can be reduced by nitrogen during the sintering process and form aluminium nitrides according to reaction (1) [11]:



An advantage of sintering aluminium and its alloy under nitrogen atmosphere is the formation of aluminium nitride which is acting as an additional strengthening factor. The presence of AlN after sintering under nitrogen atmosphere has been confirmed by the X-ray diffraction patterns (Fig. 6). The formation of aluminium nitride is an exothermic reaction which may occur if nitrogen gains a direct contact with the freshly exposed aluminium surface according to reaction (2) [11]:



To initiate the reaction between aluminium and nitrogen, a strong triple bond in the nitrogen molecule has to be broken. It requires a large source of energy which is derived from the energy released by the combined exothermic allotropic changes of Al_2O_3 [1].

The microstructure of Al4Cu alloy matrix composites consists of regular aluminium grains with copper dissolved in them and precipitates formed during cooling corresponding to

the Al-Cu phase diagram. According to the Al-Cu phase diagram, increasing the temperature of sintering above the point of eutectic transformation (548°C) promotes the formation of a liquid phase in the composite, which fills the pores and penetrates through the Al powder boundaries resulting in better consolidation [12]. The EDS point analysis with Al and Cu distribution has indicated high content of copper at the aluminium powder boundaries (Fig. 7). The composition of the precipitates is corresponding to the composition of the Al_2Cu phase (point 1). The presence of precipitates of this type and of copper dissolved in aluminium (points 2,3,4) confirms copper diffusion into aluminium occurring during the manufacturing process. As shown in Figures 7 and 8, copper addition introduced to the matrix reveals the primary grain boundaries, mainly due to the precipitation of Al_2Cu phase, which appears in lighter contrast against the background of the matrix as a continuous network spread along the Al powder particles.

The entire volume fraction of the reinforcing phase is distributed uniformly in the boundary region of the Al and Al4Cu matrix. This fairly homogenous distribution of SiC in the matrix was obtained by application of the reinforcement with particle size ($40\text{-}60\ \mu\text{m}$) similar to the size of the particles present in the matrix. The agglomeration effect of SiC particles could not be avoided in the composites containing fine SiC powder. This can be noticed in the SEM images of composites containing different percent volume fractions of SiC with particle size below $2\ \mu\text{m}$ (Fig. 8). Increasing the volume fraction of these particles has

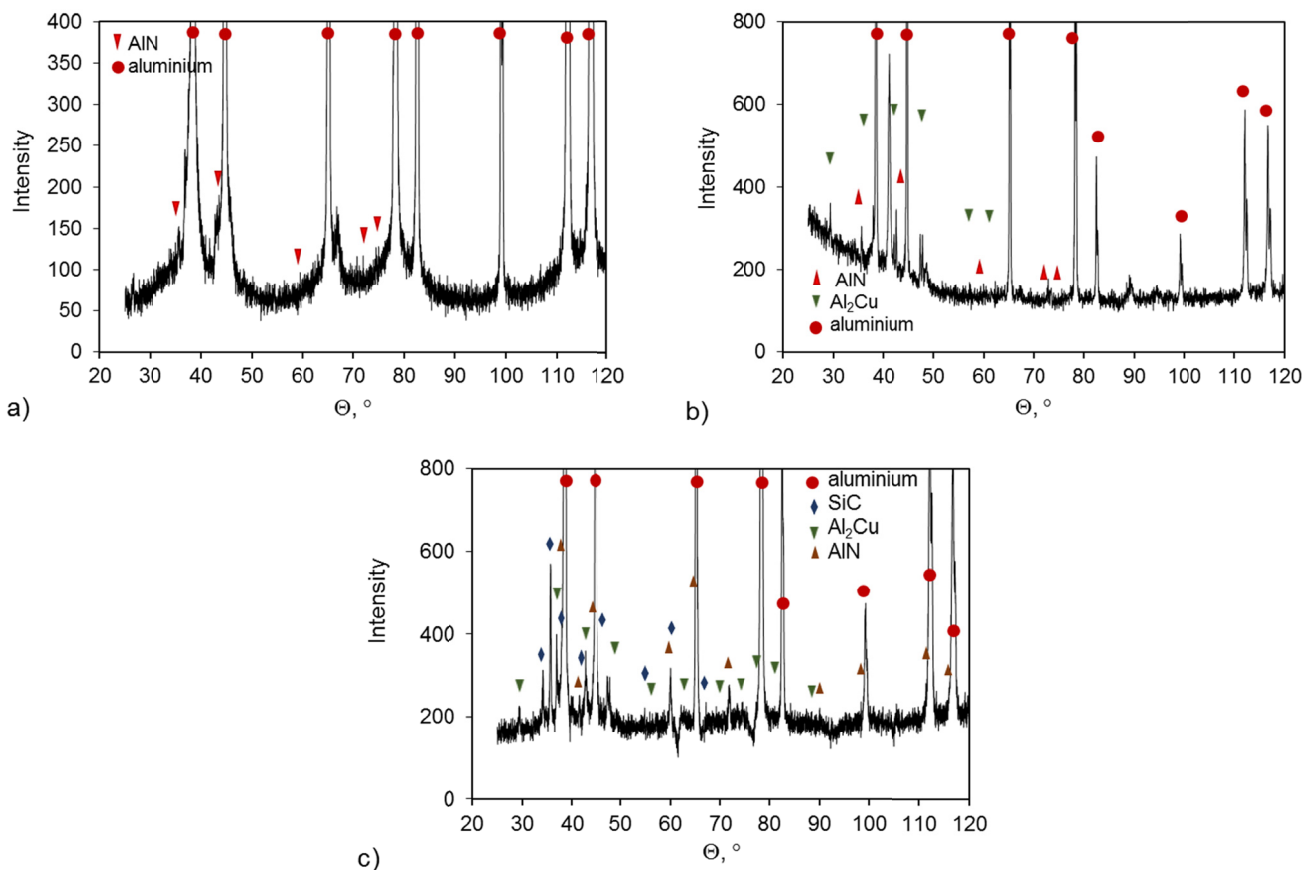


Fig. 6. XRD pattern of: a) Al matrix, b) Al4Cu matrix and c) Al4Cu + 5% SiC composite

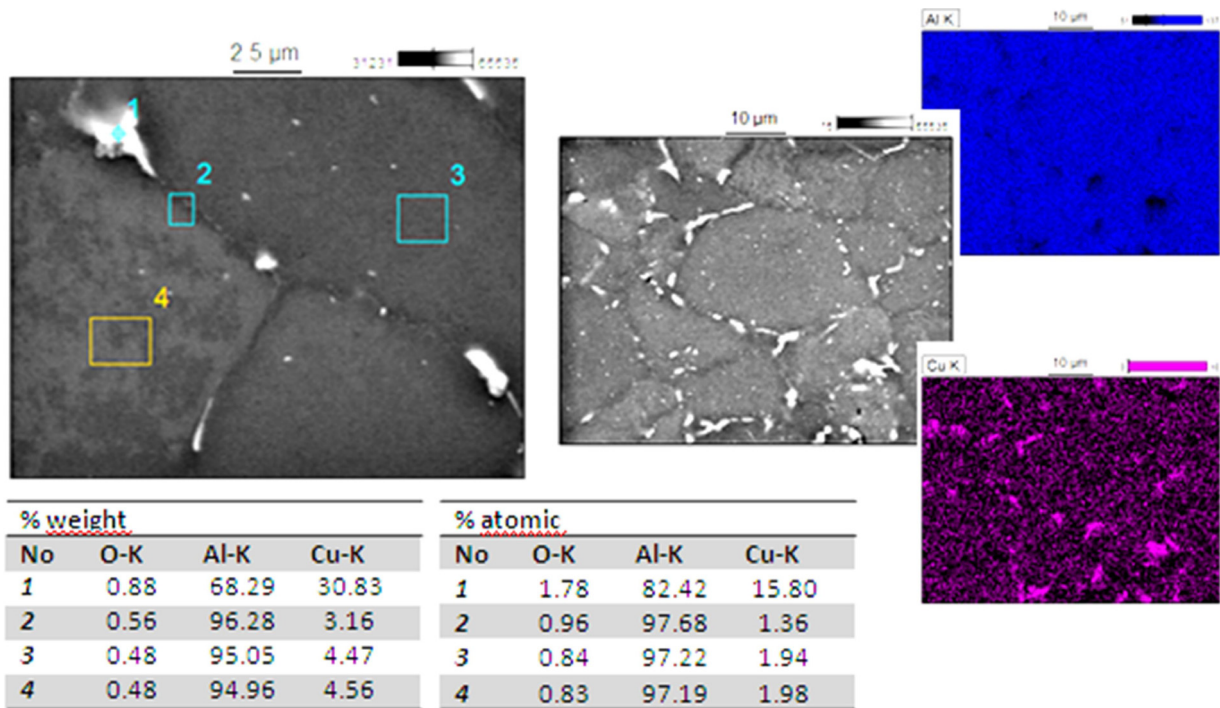


Fig. 7. Chemical analysis in micro-regions (a) and Al and Cu distribution (b) in as-sintered (2p2s, 600°C) Al4Cu alloy, SEM

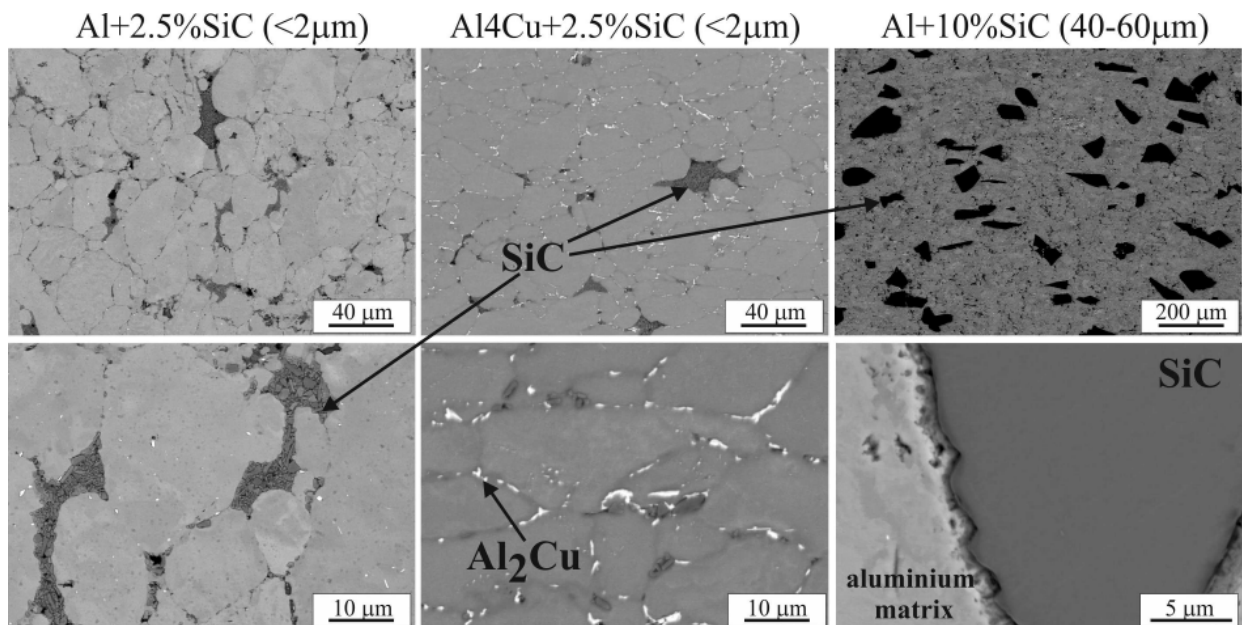


Fig. 8. Microstructure of as-sintered (2p2s, 600°C) PM Al and Al4Cu matrix composites, SEM

increased their agglomeration rate. Fine – grained SiC particles tended to segregate and agglomerate at the boundaries of Al powder particles, and it was hard to avoid this effect without the application of ball milling. TEM images of the silicon carbide particles in Al4Cu + 5% SiC composites with particle size <2 µm are presented in Figure 9.

TEM examinations of the Al4Cu matrix microstructure (Fig. 10) have revealed the locally occurring subgrain formations. As in previous studies, also now, the presence of the Al₂Cu phase was disclosed. The formation of dislocation loops and dislocation accumulations is visible in Figure 10. The penetration of

hard ceramic particles of SiC into the plastic matrix caused by mismatch in the thermal expansion coefficients of these particles and Al matrix contributes to the formation of interfacial tensile stresses, which may be sufficient to deform the matrix plastically, leading to the occurrence of high dislocation densities at the interface with the resulting strengthening of composite material [13,14]. Figures 10b and 11 show a characteristic chain-like configuration formed by aluminium oxides Al₂O₃ in aluminium matrix. The next microstructure (Fig. 12) captures the picture of nitrides which, as mentioned before, were formed during sintering under nitrogen atmosphere.

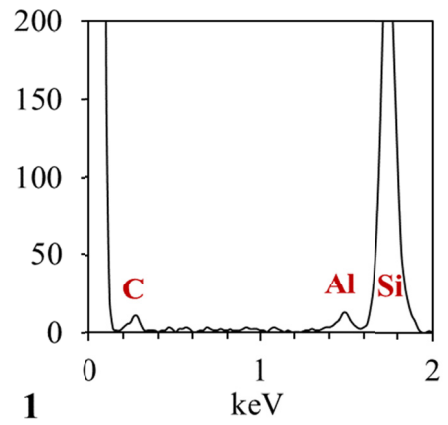
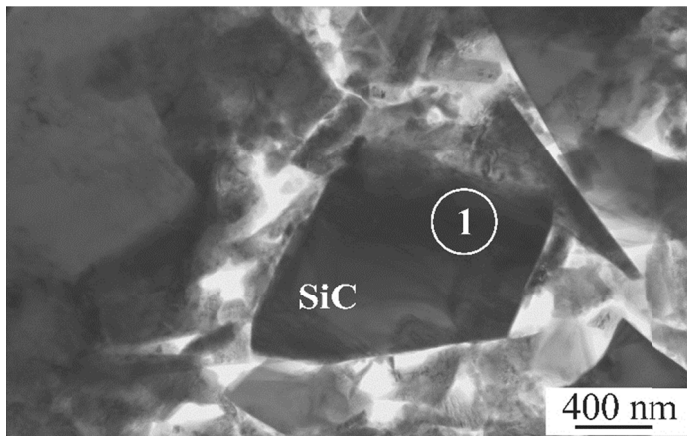


Fig. 9. TEM image of SiC particle (<math><2\ \mu\text{m}</math>)

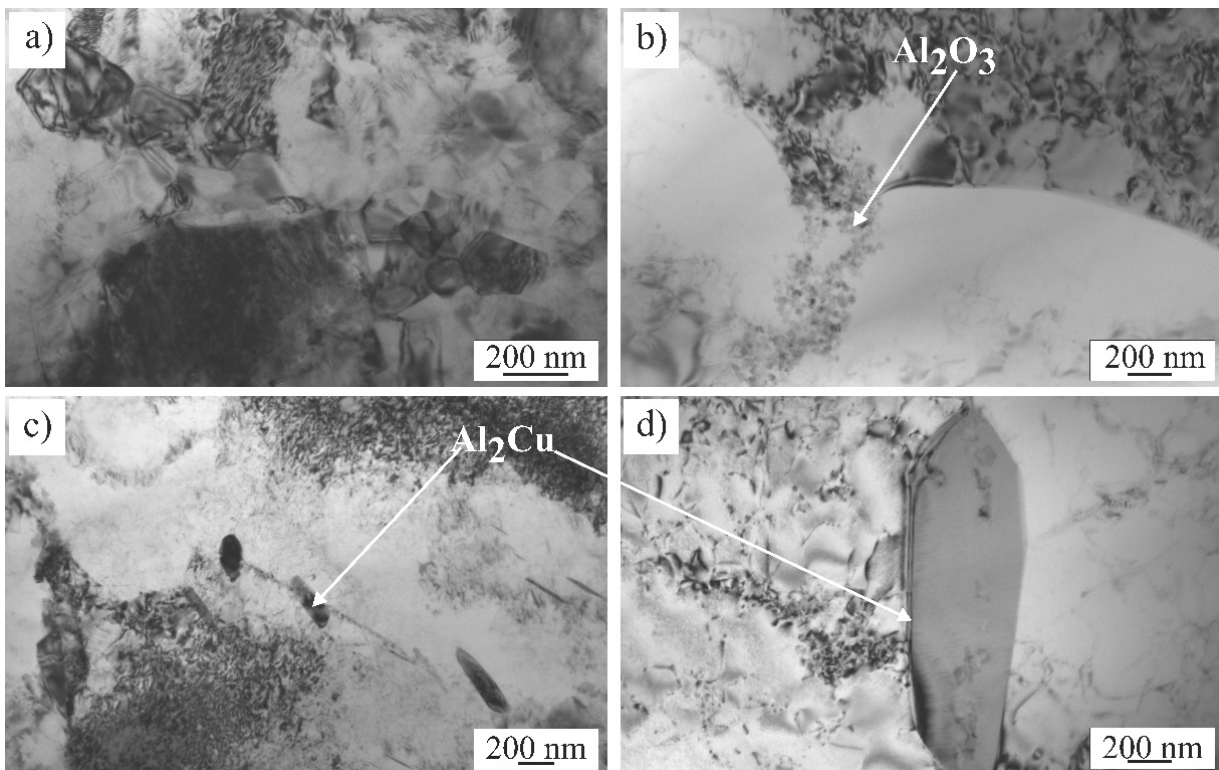


Fig. 10. Bright-field images of as-sintered (2p2s, 600°C) PM Al4Cu matrix, TEM

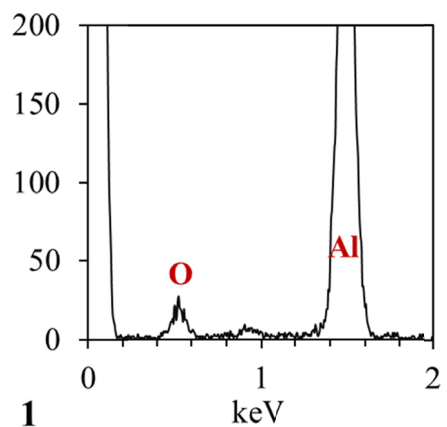
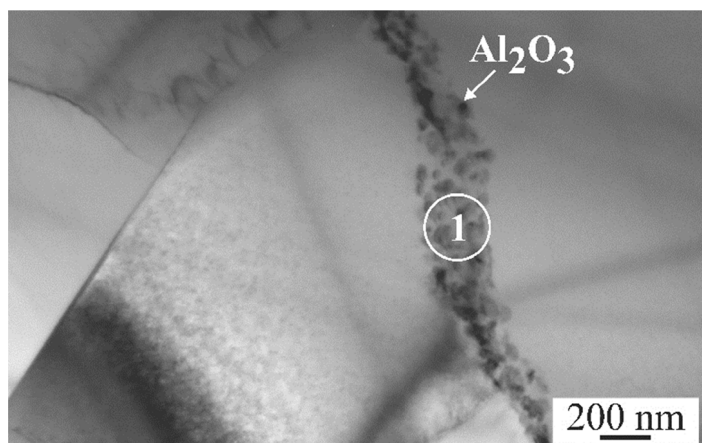


Fig. 11. TEM micrograph of as-sintered PM pure aluminium (2p2s, 600°C) with chemical analysis revealing the presence of oxides at grain boundary

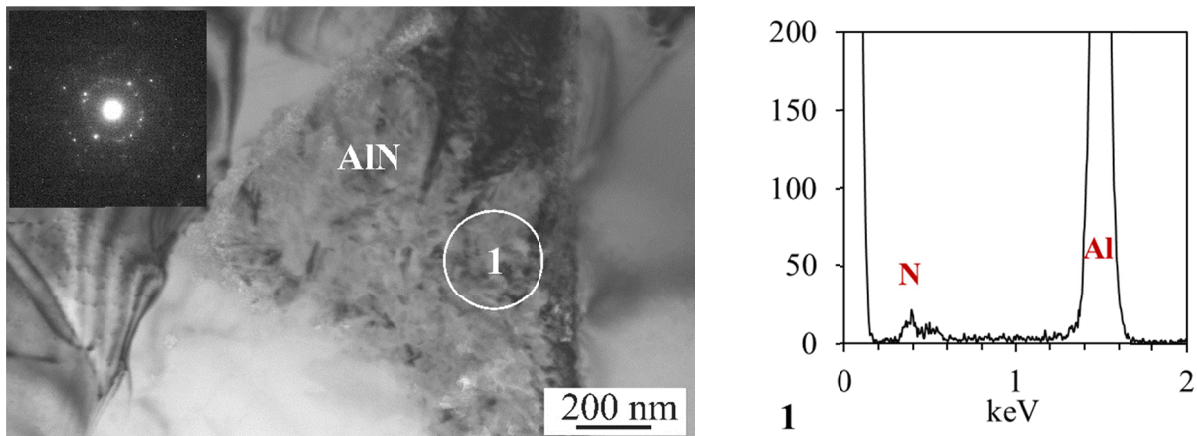


Fig. 12. TEM micrograph of as-sintered PM pure aluminium (2p2s, 600°C) with chemical analysis revealing the presence of aluminium nitrides

Figure 13 shows the microstructure and diffraction patterns of the Al_4C_3 particles occurring in Al4Cu + 5% SiC composites. The main problem observed in Al-SiC composites is related with the interfacial matrix-reinforcement reaction resulting in the formation of a brittle phase in the boundary area with the resultant drop of mechanical properties. The authors of [15] postulate that already at 650°C solid Al reacts with SiC to give Al_4C_3 according to reaction (3) [16]:

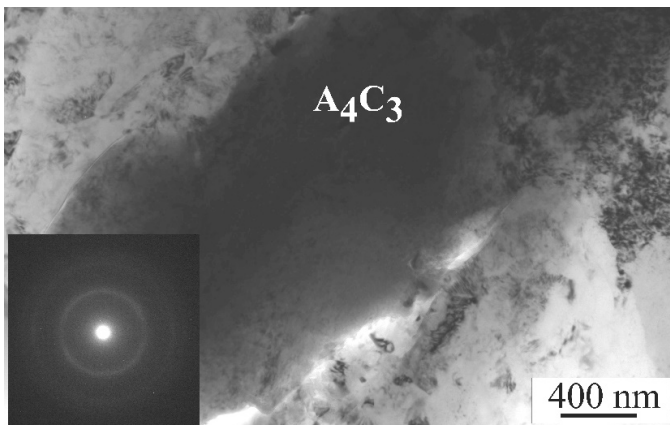
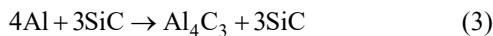


Fig. 13. TEM image of Al_4C_3 particles occurring in as-sintered (2p2s, 600°C) PM Al4Cu + 5% SiC

In the temperature range of 600-1400°C, the value of DG remains positive for the above reaction, thus restraining its spontaneous occurrence. However, in accordance with the Al-Si phase diagram, in the temperature range under consideration, silicon can dissolve into the liquid phase even when its content is very low. This will reduce the DG of the reaction to negative values, leading to the formation of Al_4C_3 [15,17]. Although the fabrication of Al-SiC composites by powder metallurgy should avoid the interfacial chemical reactions at lower temperatures and the formation of Al_4C_3 should not occur [18,19], TEM observations have indicated the presence of Al_4C_3 (Fig. 13).

As mentioned before, solid Al reacts with SiC at a temperature by 10°C lower than the melting point of pure aluminium. The sintering process was carried out at 600°C, when the gaseous atmosphere had already entered into direct contact with metallic Al followed by the immediate oxidation and heat release responsible for self-heating, which presumably caused local increase of temperature [1].

3.3. Hardness Evolution

As an example, Figure 14 shows the effect of re-pressing and re-sintering on the hardness of Al4Cu matrix composites containing various amounts of the silicon carbide particles with 2 μ m size. The Brinell hardness increases with the increasing content of SiC, and this effect is even more visible after double pressing and double sintering. As in previous case, also now, application of the additional pressing and sintering has allowed obtaining higher values of hardness. The most notable hardness growth by more than 10 units in Brinell scale was observed for composites reinforced with 5 and 7.5% of SiC. The Al4Cu matrix composite with the addition of 7.5% of SiC was characterized by the highest value of hardness reaching 71 HB. Above this silicon carbide content, hardness declined to 65 HB after double pressing and double sintering.

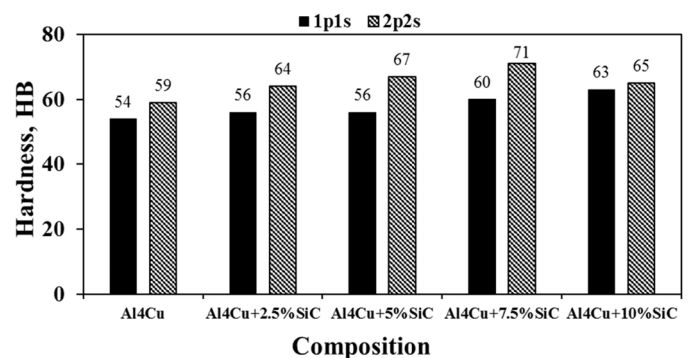


Fig. 14. The effect of process parameters on as-sintered hardness of PM Al + 4 wt% Cu matrix composites with SiC phase particles of 2 μ m size

The introduction of SiC particles into Al matrix increases the strain energy on account of the formation of dislocations at the SiC particles/ aluminium matrix phase boundary, due to the difference in thermal expansion coefficients of both these phases. Numerous dislocations stimulate the increase of hardness. The more silicon carbide particles are introduced into the aluminium matrix, the higher is the dislocation density and the resultant hardness of the composite [20,21].

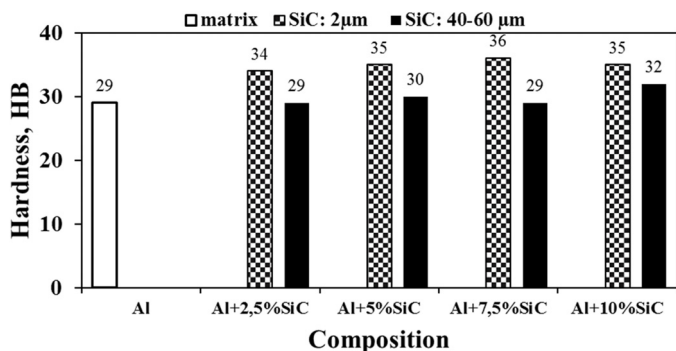


Fig. 15. As-sintered hardness of (2p2s) PM Al matrix composites as a function of the quantity and size of the SiC reinforcement particles

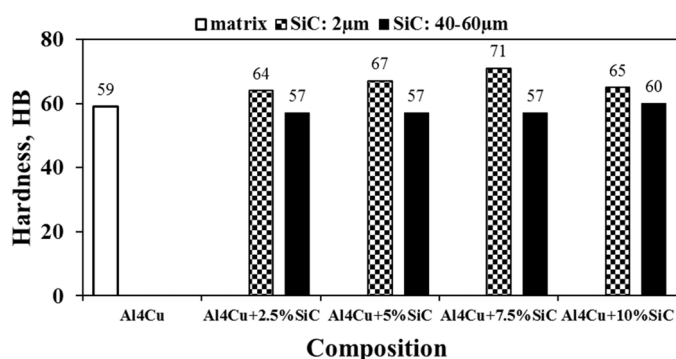


Fig. 16. As-sintered hardness of (2p2s) PM Al + 4 wt% Cu alloy matrix composites as a function of the quantity and size of the SiC reinforcement particles

Figures 15 and 16 show Brinell hardness evolution in the aluminium and Al4Cu alloy matrix composites, respectively, as a function of the chemical composition of these composites related to the particle size of the reinforcing phase. It can be clearly seen that differences in the size of the particles of the reinforcing phase exert an effect on the hardness values. Fine SiC particles confer higher hardness values to the composites compared with the particle size of 40-60 µm. In the case of aluminium matrix composites, the measured hardness is higher by about 5 HB and by 5-15 HB in the composites based on Al4Cu alloy. It should also be noted that the addition of 4% copper to aluminium matrix results in a nearly twofold increase of hardness compared to aluminum matrix composites without the addition of copper.

Higher hardness values observed in the composites reinforced with SiC particles smaller than 2 µm may be associated with greater probability of coming across the strengthening

phase during hardness test. In addition, small particles densely distributed in the matrix can form an effective barrier to the dislocation movement, which also results in increased levels of strengthening.

4. Conclusions

In this research work, Al and Al4Cu alloy composites reinforced with SiC particles were fabricated by the methods of conventional powder metallurgy. Several conclusions can be drawn from the study:

- Application of the reinforcing phase with particle size (40-60 µm) similar to the size of aluminium matrix particles resulted in a uniform dispersion of SiC in the matrix. However, segregations of the reinforcing phase appeared in the microstructure of composites containing fine SiC particles (<2 µm).
- During sintering the diffusion of Cu in Al occurs. Al reacts with Cu forming Al₂Cu phase on the grain boundary.
- During compaction, the oxide coating formed on the surface of the matrix powder particles can break which increases the interfacial bonding strength.
- Sintering under nitrogen atmosphere induces the formation of AlN.
- Although the investigated composites were fabricated by the PM route, which is a solid-state fabrication process, the formation of an unfavourable Al₄C₃ phase at the SiC/Al matrix interface was observed. This fact requires further studies.
- Double pressing and double sintering increase the composite hardness. The composite hardness also tends to increase with the increasing SiC content and is higher for the composites with fine SiC particles and copper addition introduced to the matrix due to the formation of Al₂Cu and Cu diffusion to the aluminium matrix.

REFERENCES

- [1] T. Pieczonka, Powder Metallurgy Processing of Aluminium in: Polish metallurgy 2006-2010 in time of the worldwide economic crisis, Committee of Metallurgy of the Polish Academy of Sciences-Kraków: Publishing House AKAPIT 2010.
- [2] V. Jeevan, C.S.P. Rao & N. Selvaraj, International Journal on Mechanical Engineering and Robotics (IJMER) **1** (2), 34-38 (2013).
- [3] M.K. Surappa, Sadhana **28** (1,2), 319-334 (2003).
- [4] S. Charanjit, S. Jagtshwar, Journal of Mechanical and Civil Engineering (IOSR-JMCE), **11** (3), 12-17 (2014).
- [5] A. Fathy, A. Sadoun, M. Abdelhameed, The International Journal of Advanced Manufacturing Technology **73**, 1049-1056 (2004).
- [6] A. Mahamood, A. TurkiMayyas, A. Alrashdan, M.T. Hayajneh, J. Mater. Sci. **43**, 5368-5375 (2008).
- [7] F. Bedir, Science Direct, Materials and Design **28**, 1238-1244 (2007).

- [8] B. Leszczyńska-Madej, Archives of Metallurgy and Materials **58** (1), 43-48 (2013).
- [9] Ch. Sun, R. Shen, M. Song, Journal of Materials Engineering and Performance **21** (3), 373- 381 (2012).
- [10] F. Tang, I.E. Anderson, S.B. Biner, J. Light Met. **2** (4), 201-214 (2002).
- [11] G.B. Shaffer, B.J. Hall, Metallurgical and Materials Transactions **A33**, 3279-3284 (2001).
- [12] B. Ogel, R. Gurbuz, Materials Science and Engineering A **301**, 213-220 (2001).
- [13] A.M. Samuel, A. Gotmare, F.H. Samuel, Compos. Sci. Technol. **53**, 301-315 (1995).
- [14] A. Sunday, J.A. Omotoyinbo, D.O. Folorunso, Leonardo Electronic Journal of Practices and Technologies **18**, 9-16 (2011).
- [15] C. Bartuli, F. Carassiti, T. Valente, Advanced Performance Materials **1**, 231-242 (1994).
- [16] A. G.Baker, International Journal of Advanced in Applied Sciences (IJAAS) **2**, 2, 67-72 (2013)
- [17] T. Iseki, T. Kameda, T. Maruyama, Journal of Materials Science **19**, 1692-1698 (1984).
- [18] H.M. Zakaria, Ain Shams Engineering Journal **5**, 831-838 (2014).
- [19] S. Hao, J. Xie, A. Wang, M.Fang, Materials Transactions **55**, 5, 750-753 (2014).
- [20] S.W. Kim, U.J. Lee, S.W. Han, D.K. Kim, K. Ogi K, Composites Part B **34**, 8, 737-745 (2003).
- [21] T. Das T, P.R. Munroe, S. Bandyopadhyay, J. Mater. Sci. **31**, 20, 5351-5361 (1996).