Materials Research Proceedings 41 (2024) 696-705 https://doi.org/10.21741/9781644903131-77

Effect of ball milling processing on mechanical properties of extruded aluminum-graphene-composites with commercial and self-synthesized graphene sources

NEGENDANK Maik[1,a *], HOERNSCHEMEYER Jens[1,b], JAIN Nishant[2,c] and MUELLER Soeren[1,d]

[1]Extrusion Research and Development Center, TU Berlin, Gustav-Meyer-Allee 25, 13355 Berlin, Germany

[2]Chair of Advanced Ceramic Materials, Hardenbergstr. 40, 10623 Berlin, Germany

[a]maik.negendank@strangpressen.berlin.de, [b]jens.hoernschemeyer@campus.tu-berlin.de, [c]nishant.jain@ceramics.tu-berlin.de, [d]soeren.mueller@tu-berlin.de

Keywords: Aluminum Graphene Composites, Oxalic Acid Exfoliated Graphite, Ball Milling, Extrusion, Mechanical Properties

Abstract. In this study the effect of ball milling processing on the mechanical properties of extruded aluminum-graphene-composites was investigated. A commercial and a self-synthesized graphene source was applied respectively. It was found that rods of extruded high speed ball milled (HSBM) materials showed bad surface quality with massive cracks. The extrusion loads in indirect extrusion were 100% higher for HSBM material compared to material that was ball milled at lower rotation speed (LSBM). Investigations of mechanical properties revealed that for HSBM material TYS was increased 92% and UTS 118% compared to LSBM. Microhardness was also found to increase by up to 210% for HSBM material containing 1% graphene. However, since pure aluminum processed under same conditions also featured a drastic increase in hardness of 167%, it can be concluded that work hardening of the pure aluminum matrix seems to be the main strengthening mechanism. Furthermore, graphene agglomerates could be found locally in all extruded samples.

Introduction

Graphene is a planar material consisting of sp^2-hybridized carbon layers. Its first synthesis was reported in the year 2004 [1]. Due to the exceptional properties of monolayer graphene, such as extremely high strength (130GPa) and elastic modulus (1TPa), graphene is very attractive to be applied as strengthening additive for Metal-Matrix-Composites (MMCs) [2]. Problematic is the fact that due to strong Van der Waals forces, graphene layers tend to agglomerate [3]. However, significant improvements in mechanical properties of composites can only be achieved when graphene is well exfoliated, distributed homogeneously in the matrix and the graphene source is of good quality (low number of layers and defects). In a previous study the authors applied short duration disc milling as a time and thus cost-efficient approach to manufacture aluminum-graphene-composites [4]. The results showed increased TYS by 16%, UTS by 27% and microhardness of up to 49%. However, in the literature several studies on ball milling as a production step for such composites can be found. Often ball milling was found to be beneficial for dispersion of graphene nano particles when the milling parameters are chosen accordingly [5]. In ball milling the radial component of the collision force (the compression force) of the milling balls with the aluminum powder particles can result in their flattening, fragmenting or cold-welding. While the tangential component of the collision force (the shearing force) can contribute to a better dispersion of GNPs as graphene layers that are attached to another initially, might be separated through shearing [6]. Zhang et al. [7] applied ball milling with a rotation speed of 350rpm

for up to 24h with a ball-to-powder weight ratio of 20:1. After extrusion at 300°C with an extrusion ratio of R=10:1 TYS as well as in UTS were improved by 50%. Jiang et al. [5] performed shift-speed ball milling consisting of a long-term milling step at low rotation speeds of 200rpm and a short-term step at 500rpm. Again, a ball-to-powder ratio of 20:1 was selected, and results showed improvements in TYS of 24% and in UTS of 20%. Zheng et al. [8] achieved 166% higher TYS and 116% higher UTS by applying 10h of low milling speeds (100rpm) followed by 2h at 300rpm (ball-to-powder ratio 16:1) and extrusion at 450°C with R=25:1.

In the current study aluminum-graphene-composites with commercial as well as self-synthesized graphene sources should be manufactured via powder metallurgical route. Mechanical stirring, ball milling and indirect extrusion processing were applied to investigate the effects of processing conditions on the composites' mechanical properties. Another aim was to study the differences in composite properties when commercially available GNPs or a graphene source synthesized by the authors was applied respectively.

Materials and Methods

In this study gas atomized pure aluminum (99.7%) powder was applied as matrix material. It was provided by TLS Technik GmbH & Co. KG, Germany. Particle size distribution was given in a prior study [4], with mean particle size being D_{50}=49µm. Two different graphene sources were applied. The first was commercial graphene nano platelets (GNP) provided by Alfa Aesar® (AA-GNPs). The second source was graphene that was synthesized by the chair of advanced ceramic materials of TU Berlin (Prof. Gurlo). Synthesis applied disc milling of fine graphite with oxalic acid. Hence, throughout this study the second source will be named oxalic acid exfoliated graphite (OAEG). A detailed study on the synthesis and characterization of OAEG will be published elsewhere soon. AA-GNPs have already been characterized in [4].

Extrusion billets for the current study here were prepared via powder metallurgical processing route. In dry (as-received) condition graphene particles formed agglomerates due to strong Van der Waals forces. Hence, in a first step graphene was soluted in a flask with ethanol. To improve graphene exfoliation and reduce number and size of agglomerates, the solution was sonicated with a sonification finger for 10min during simultaneous electromagnetic stirring. 1.5wt.% stearic acid as a process control agent was applied and together with pure dry aluminum powder was filled into an Eirich mixer type EL1. Afterwards, the liquid graphene/ethanol mixture was slowly added. Batches with graphene contents of 0wt.%, 0.25wt.%, 0.5wt.% and 1.0wt.% were produced with the commercial AA-GNPs. Regarding the OAEG, contents of up to 0.5wt.% were prepared only, due to insuffient amount of OAEG-powder. Additionally, prior results indicated decreasing properties for graphene contents above 0.5wt.% [4, 9]. Then the powder mixture was stirred for 6min at a rotation speed of 1800rpm. The mixed powders were then dried in a vacuum furnace at 50°C for 8h. After that powders were ball milled in a planetary mill (Fritsch Pulverisette 5) at different milling durations (1h, 4h, 8h) and rotation speeds (100rpm, 300rpm). Steel balls with a diameter of 12mm were applied for milling at a ball to powder weight ratio of 10:1. At the high rotation speed of 300rpm the milling process had to be conducted in stints due to strong heat generation. Hence, milling was conducted for 15min followed by a pause of 15min respectively. After ball milling, powders were degassed in a chamber furnace at 400°C in argon atmosphere to remove the stearic acid. Powder particle morphology in dependence of ball milling conditions were investigated in SEM (JEOL 640). Particle size could not yet be determined due to a technical defect of the particle size analyzer.

Milled powders were compacted into discs in a uniaxial press at room temperature. 32g powder were used for one each disc, resulting in a height of approximately 20mm. Compaction was conducted with a force of 150kN (pressure of 230MPa).

Extrusion processing was conducted in indirect extrusion mode on a 0.5MN extrusion press at the Extrusion Research and Development Center of TU Berlin. Three compacted discs were

stacked respectively for one billet. Discs and extrusion tools were heated to extrusion temperature of 350°C in a chamber furnace. Soaking time for Al-graphene-compacts was 45min to 60min. The container with diameter of 30mm was heated to the same temperature. A conic extrusion die with an orifice diameter of 8.0mm and a die angle of 2α=150° was applied for the extrusions. Ram speed was set to 3mm/s. For each condition (GNP-type, GNP-content, milling duration and milling speed) only one rod was extruded respectively.

After extrusion rod surface quality was evaluated and compared. Then, sections for mechanical testing were cut from the center of the rods towards the end. Tensile testing was performed on a MTS 810 testing machine at a strain rate of $3 \cdot 10^{-4} s^{-1}$. Characterization of GNP-dispersion was conducted by optical microscopy on rod cross sections after etching with Dix-Keller's etchant.

Results and discussion

The effects of ball milling parameters on aluminum as well as aluminum/graphene particles were investigated via SEM. The initial aluminum powder was of spherical shape [4]. Fig. 1 shows that after ball milling for 4h at 100rpm Al-particles were still predominantly round-shaped. However, their surface was rough and additionally some more plate-like shaped particles were also found. After a longer milling duration of 8h at 100rpm nearly all particles were deformed into plates. HSBM at 300rpm for 1h resulted in a significant reduction of the thickness of the plate-shaped particles as they were flattened significantly. After 4h of ball milling at 300rpm the particle morphology seemed to be unchanged but flattened aluminum particles seemed to be stacked and attached to each other. This indicates that cold-welding might have occurred.

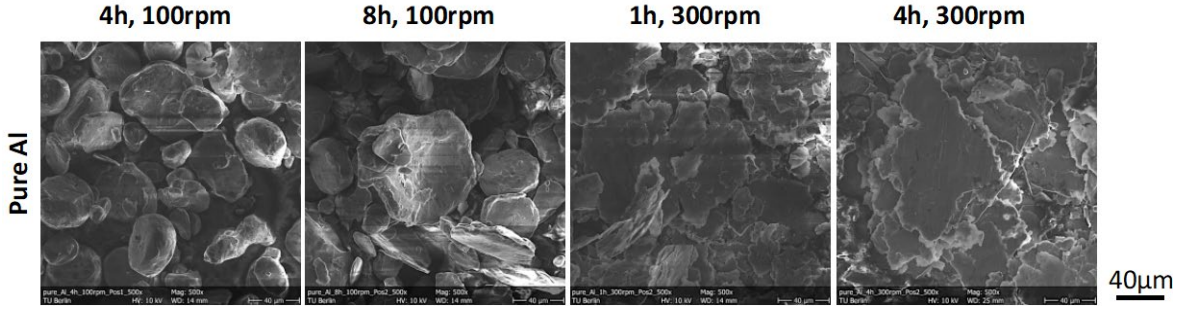

Fig. 1: SEM images of particle size and morphology of pure aluminum powders in dependence of ball milling conditions

Ball milled composite powders with 0.5% AA-GNPs and 0.5% OAEG were also investigated with SEM (Fig. 2). Graphene particles are indicated with arrows exemplarily. It was revealed that after ball milling AA-GNPs as well as OAEG were found to be attached to the surface of Al-particles. The commercial AA-GNPs seemed to be of bigger lateral size. Furthermore, they were found to be stacked on top of each other more often than the OAEG after same milling conditions. Hence, it can be concluded that OAEG are finer and better dispersed than AA-GNPs. Both factors should be favorable for improving mechanical properties of aluminum/graphene composites [3]. However, after 4h of HSBM at 300rpm, no graphene particles were found on the surface of aluminum powder particles. Hence, they must have been either reduced in size dramatically or dispersed into the aluminum particles during HSBM.

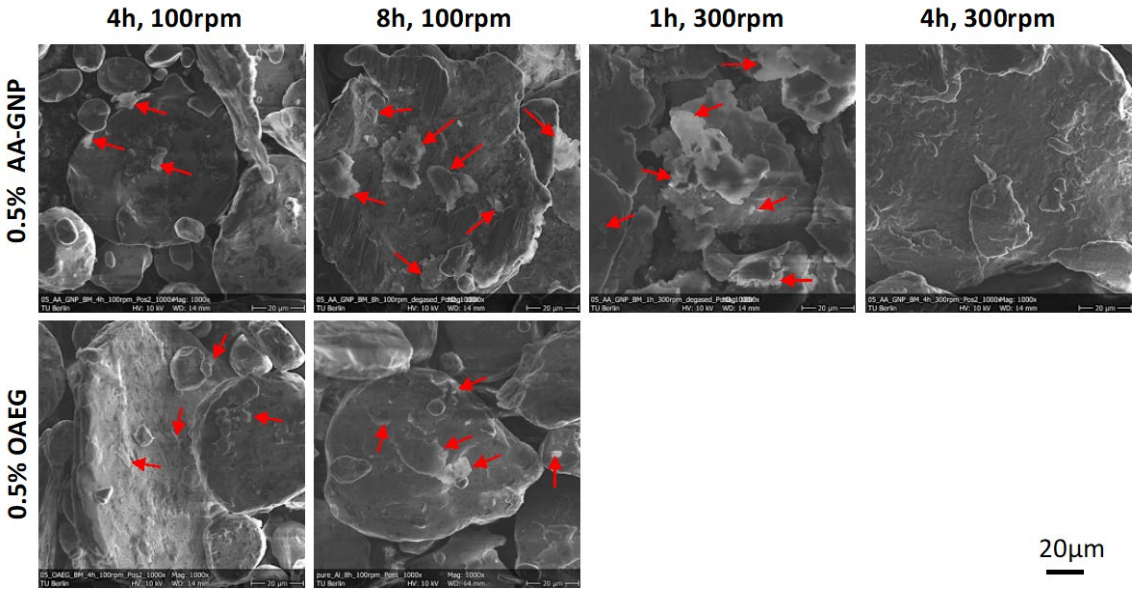

Fig. 2: SEM pictures of 0.5% Al/graphene composite powders after ball milling with different milling parameters and degassing (graphene exemplarily marked with arrows)

Next the effects of ball milling conditions (energy input), GNP-content and GNP-type on the extrusion load will be described. The extrusion loads (peak force at the beginning of the indirect extrusion process) are displayed in Fig. 3. It can be noted that the predominant factor for the extrusion load is the rotation speed during ball milling. At low rotation speeds of 100rpm extrusion forces were around 200kN. In fact, at the lower milling duration of 4h forces between 172kN (0.5% OAEG) and 191kN (0.25% OAEG) were observed. At longer milling duration of 8h, similar but slightly higher extrusion loads between 172kN (1.0% AA-GNPs) and 213kN (0.5% AA-GNPs) were found. The slightly increasing tendency could be the result of stronger work hardening of aluminum particles due to longer milling duration and thus increased material deformation. The effect of graphene content on extrusion load was not significant in these cases. On the other hand, for extrusion of the HSBM-materials a significant increase in extrusion load was found for all extrusions. For the 1h HSBM milled materials extrusion loads between 426kN (0.25% AA-GNPs) and 483kN (0.5kN) were found. Hence, extrusion loads doubled due to HSBM. For the longer milling duration of 4h at 300rpm the results tended to decrease. Extrusion loads between 309kN (0.5% AA-GNP) and 388kN (pure Al) were measured in this case.

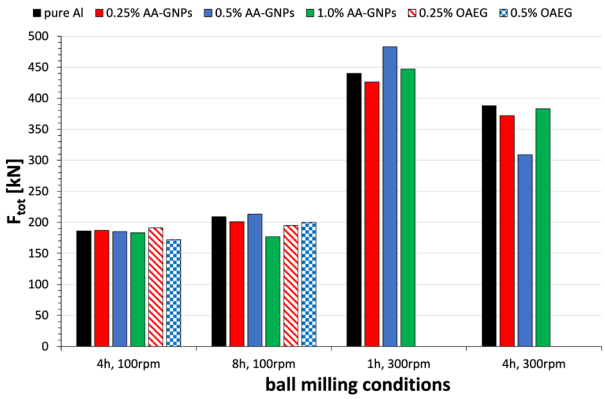

Fig. 3: Effect of ball milling conditions, graphene type and graphene content on peak extrusion loads in indirect extrusion processing

After extrusion the quality of extruded rods was inspected. Rods of low-speed ball milled material (LSBM) (milled at 100rpm) showed some grooves only. However, all rods of the HSBM-

material including those of pure aluminum featured massive surface cracks. Fig. 4a visualizes the effect of ball milling conditions for rods with 0.5% AA-GNP content. Fig. 4b on the other hand illustrates the effect of different AA-GNP contents on rod surface quality for composite materials that were ball milled for 8h at 100rpm. It can be noted that rod surface quality decreased with increasing GNP content. This effect was also observed in previous studies for disc milled and indirectly extruded Al/GNP composites [4] as well as for mechanically mixed and directly extruded composites [9].

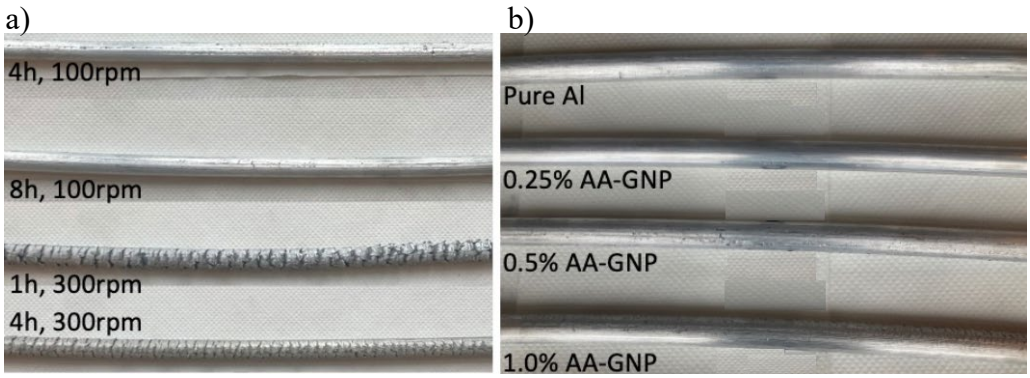

Fig. 4: Rod surface quality in dependence of a) applied ball milling conditions for 0.5% AA-GNP composites b) AA-GNP content (ball milled for 8h at 100rpm)

To characterize the effect of different ball milling parameters on the composites' mechanical properties, tensile tests as well has microhardness testing were performed. As noted previously, due to surface cracking, samples for tensile testing could mostly be prepared for LSBM-material only. The tensile yield strengths (TYS) as well as the ultimate tensile strengths (UTS) and fracture strains (E_{fr}) are summarized in Table 2 and visualized in Figures 5a and 5b respectively.

Table 2: Summary of tensile test results

ball milling conditions	pure Al			0.25% AA-GNPs			0.5% AA-GNPs			1.0% AA-GNPs			0.25% OAEG			0.5% OAEG		
	TYS [MPa]	UTS [MPa]	E_{fr} [%]	TYS [MPa]	UTS [MPa]	E_{fr} [%]	TYS [MPa]	UTS [MPa]	E_{fr} [%]	TYS [MPa]	UTS [MPa]	E_{fr} [%]	TYS [MPa]	UTS [MPa]	E_{fr} [%]	TYS [MPa]	UTS [MPa]	E_{fr} [%]
4h, 100rpm	81±1	114±1	36±6	78±1	112±1	30±5	82±1	114±1	24±1	79±4	112±1	22±3	85±2	118±2	21±1	80±1	115±1	28±1
8h, 100rpm	90±6	125±1	28±1	84±1	124±1	24±1	86±1	128±1	25±3	88±4	124±1	20±1	88±1	127±1	25±3	86±1	125±1	27±1
1h, 300rpm	-	-	-	150±5	244±1	7±1	-	-	-	-	-	-	-	-	-	-	-	-

For composites being ball milled at 100rpm for 4h prior to extrusion, TYS values between 78MPa and 85MPa were found. The pure aluminum reference featured a TYS of 81MPa. UTS values for these composites were between 112MPa (1% AA-GNP) and 118MPa (0.25% OAEG). The UTS of the pure Al sample was 114MPa.

Samples that were milled at 100rpm for a longer duration of 8h featured slightly higher values. The TYS values were found in the range between 84MPa (0.25% AA-GNPs) and 88MPa (0.25% OAEG) with pure Al at 90MPa. UTS values were between 124MPa and 128MPa with pure Al being at 125MPa. Thus, TYS increased by up to +11% and UTS by up to +7%. Further, it can be learned that for LSBM composites, the effect of graphene content as well as the applied graphene source (commercial AA-GNPs and self-synthesized OAEG) did not have a strong effect on TYS and UTS. Additionally, the strengths values of LSBM-material are similar to these gained after short term disc milling in a prior study [4].

However, from the extruded rod containing 0.25% AA-GNPs that was initially HSBM for 1h at 300rpm, despite some minor surface cracks, it was possible to manufacture samples for tensile testing. For these samples significantly higher strengths of TYS=150MPa and UTS=244MPa were observed. Thus, the HSBM samples have a 92% higher TYS and a 118% higher UTS when being compared to the pure Al samples ball milled at 100rpm for 4h.

Regarding the fracture strain it was observed that the increases in strengths came at the cost of lower fracture strain and thus ductility. Composites with 0.25% AA-GNPs showed a slight decrease from E_{fr}=30% to E_{fr}=25% when LSBM duration was varied from 4h to 8h. More drastically the fracture strain reduced to E_{fr}=7% when HSBM at 300rpm was conducted for 1h.

Sections from all extruded rods including those with severely cracked surfaces were tested to determine the microhardness. The results are summarized in Table 3 and visualized in Fig. 6. Very similar to the observed tendencies of tensile testing results, microhardness values for rods of LSBM-material were between 36HV to 37HV when milling duration was 4h. Increasing milling duration to 8h resulted in slightly higher microhardness values between 39 and 42HV, whereas 42HV was found for the 0.5% AA-GNP composite rod. There was no significant effect of GNP-type and GNP-content on the microhardness of LSBM material. Again, these values are in good comparison with prior results of short-duration disc milled Al/graphene-composites [4]. However, when being compared to values of 4h LSBM, processing via 4h of HSBM increased hardness values substantially. Improvements by up to 159% (in case of 0.5% AA-GNPs) to values between 75HV and 90HV (1h, 300rpm) and even further by up to 210% (in case of 1.0% AA-GNPs) to values between 95HV to 115HV in case of 4h HSBM were found. HSBM also significantly increased microhardness of pure aluminum by 167%. Hence, it might be concluded that work hardening of aluminum particles during the milling process was the main strengthening mechanism and not the addition of graphene particles. An upcoming study will focus on improving rod surface quality during extrusion. Then it can be verified, if the relationships between ball milling parameters and microhardness found in the current study show the same tendency in tensile tests.

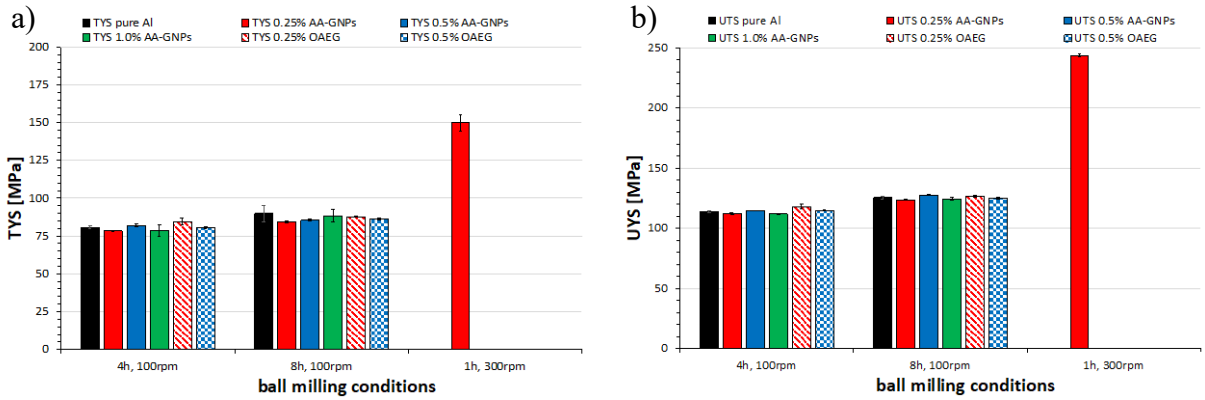

Fig. 5: Effects of ball milling conditions, graphene content and graphene type on a) Tensile yield strength (TYS) b) Ultimate tensile strength (UTS) of Al/graphene composites

Table 3: Microhardness (Vickers) of extruded Al/graphene composites in dependence of ball milling conditions, values in HV0.5

composite	ball milling conditions			
	4h, 100rpm	8h, 100rpm	1h, 300rpm	4h, 300rpm
pure Al	36±1	39±1	84±2	96±2
0.25% AA-GNPs	38±1	39±1	75±1	95±3
0.5% AA-GNPs	37±1	42±3	90±5	96±2
1.0% AA-GNPs	37±2	41±1	77±2	115±2
0.25% OAEG	37±1	39±1	-	-
0.5% OAEG	36±1	39±1	-	-

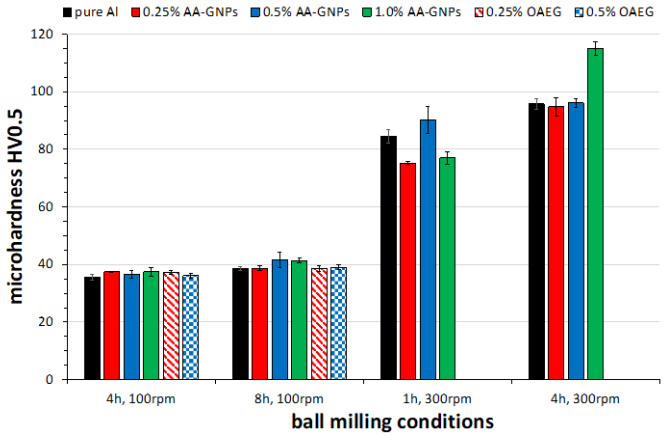

Fig. 6: Effects of ball milling conditions, graphene content and graphene type on rod microhardness

Since a homogeneous dispersion of graphene particles in the pure-Al matrix is important for significant improvements in strengths of composites, the dispersion on extruded rod cross sections was investigated by optical microscopy. The results are given at high microscope magnification of 1000x in Fig. 7 and for overview purposes at a lower magnification of 50x in Fig. 8.

At higher magnification (1000x) graphene particles (dark particles in the images) seemed to be relatively well dispersed in the pure-Al matrix even for high contents of 1.0% AA-GNPs. For the rods of LSBM materials (100rpm) there was no significant effect of milling duration on the graphene dispersion. Furthermore, the two different graphene sources of AA-GNPs and OAEG seemed to be dispersed similarly at same contents. However, after HSBM for 1h graphene particles seemed to have aligned close to each other in a meandric shape. After 4h of HSBM graphene particles were not visible in matrix anymore. It seems that longer duration for HSBM of 4h at 300rpm reduced the size of graphene particles significantly, so that they are longer visible in optical microscopy.

Fig. 8 shows that at lower magnification graphene agglomerates (black particles) can be found locally in almost all of the rod cross sections. Agglomerates are known to be detrimental for mechanical properties of composites as they might act as sites for crack initiation under tensile loading. It has to be concluded that the processing route of sonication, intensive mechanical stirring, ball milling and extrusion was not sufficient to fully dissolve preexisting (due to Van der Waals forces) graphene agglomerates. Hence, in an upcoming study the effect of additional shear deformation on the graphene dispersion and the mechanical properties will be investigated. During significant shearing, graphene layers could potentially be “sheared off” from one another. Thus, shearing would be beneficial for graphene dispersion as agglomerates may be dissolved.

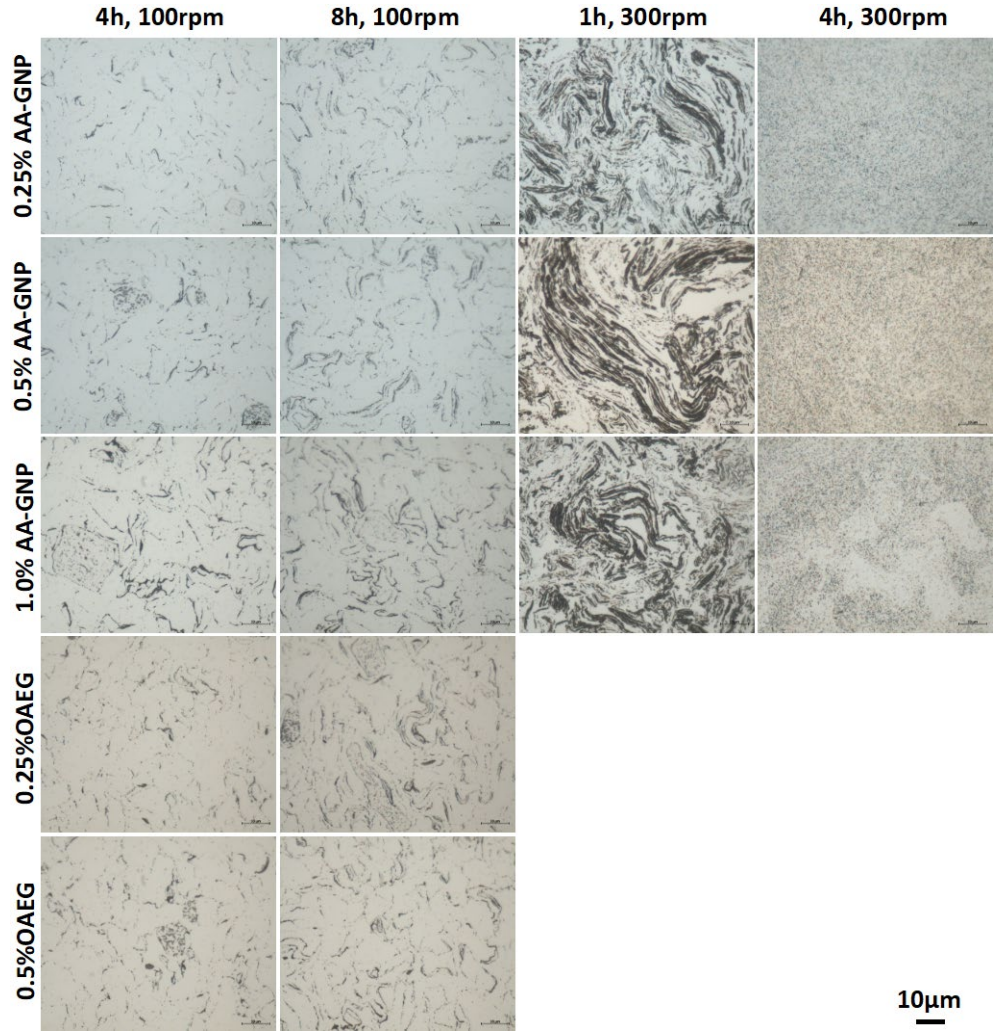

Fig. 7: OM-images of composite rod cross sections at microscope magnification of 1000x

In order to investigate if during ball milling or extrusion processing oxidation of aluminum powder or formation of Al_4C_3 phase might have occurred, XRD phase analysis (measured with Bruker D8 advanced diffractometer) was conducted exemplarily. XRD was conducted on the sample with the highest strength (0.25% AA-GNPs, 1h, 300rpm) as well as on the sample with highest overall microhardness (1.0% AA-GNPs, 4h, 300rpm). The diffraction patterns are given in Fig. 9. In case of the sample with highest microhardness besides aluminum no other peaks were detected. In case of the specimen with highest microhardness peaks of aluminum oxide (cubic Al_2O_3) were found. Hence, it seems that at least in this case during HSBM for 1h with significant heat development in atmospheric environment, oxidation of aluminum powder occurred to some extent. The Al_4C_3-phase did not appear in the patterns and thus, did not seem to have formed during processing.

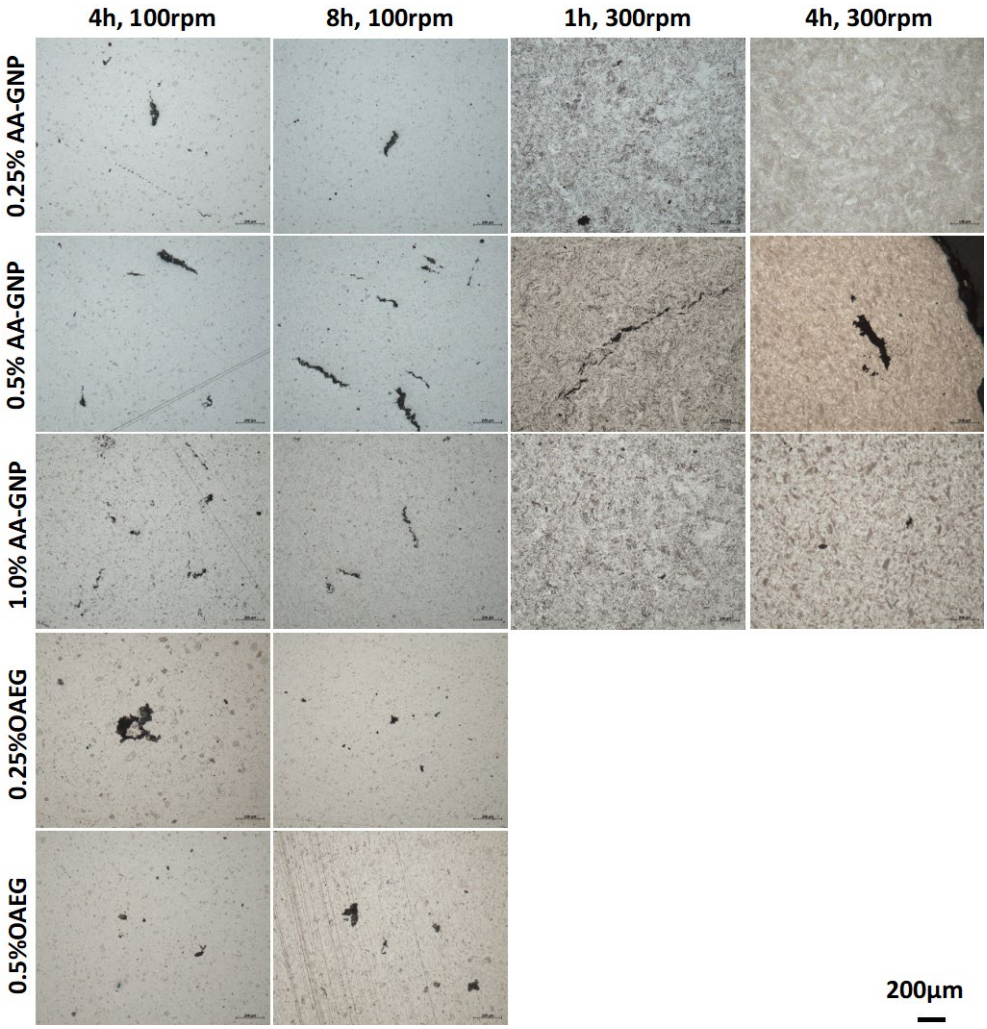

Fig. 8: OM-overview images of composite rod cross sections at microscope magnification of 50x

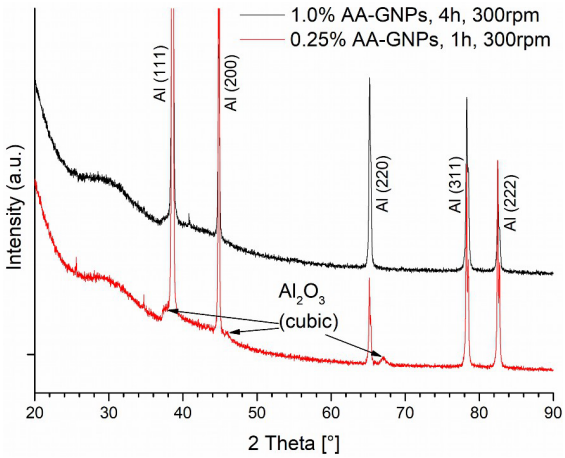

Fig. 9: XRD pattern for extruded rod materials of 0.25% AA-GNPs ball milled for 1h at 300rpm and 1.0% AA-GNP milled 4h at 300rpm

Conclusions

In this study a powder metallurgic approach of ball milling and indirect extrusion processing was performed to investigate the effects of processing parameters on the mechanical properties of extruded aluminum-graphene-composites. The following conclusions can be drawn:

- HSBM increased extrusion loads in indirect extrusion by about 100% compared to LSBM.
- HSBM resulted in bad rod surface quality (massive surface cracking).
- HSBM increased TYS by 67% and UTS by 95% but decreased fracture strain significantly.
- Higher graphene contents did not improve strengths but decreased fracture strain.
- HSBM increased microhardness by 167% for pure Al and 210% (1% AA-GNP-composite)
- Graphene agglomerates were found in all extruded rod cross sections.
- No significant differences in mechanical composite properties between commercial AA-graphene and self-synthesized OAEG were found.

Acknowledgements

The authors like to thank Zeynep Alici (chair of advanced ceramics, TU Berlin) for synthesis of OAEG for this study as well as Delf Kober (chair of advanced ceramics, TU Berlin) for conducting XRD phase analysis. This project was founded by the German Research Foundation (DFG) (grant number 426183735).

References

[1] K.S. Novoselov et al., Electric field effect in atomically thin carbon films, Science 306 (2004) 666–669. https://doi.org/10.1126/science.1102896

[2] C. Lee et al., Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene, Science 321, (2008) 385–388. https://doi.org/10.1126/science.1157996

[3] F. Chen et al., Graphene-Reinforced Aluminum Matrix Composites: A Review of Synthesis Methods and Properties, The Journal of The Minerals, Metals & Materials Society (TMS) 70 (2018) 837-845. https://doi.org/10.1007/s11837-018-2810-7

[4] M. Negendank et al., Effects of disc milling and indirect extrusion processing on mechanical properties of aluminum-graphene-composites with commercial GNPs, Materials Research Proceedings 28 (2023) 455-466. https://doi.org/10.21741/9781644902479-50

[5] Y. Jiang et al., Tailoring the structure and mechanical properties of graphene nanosheet/aluminum composites by flake powder metallurgy via shift-speed ball milling, Composites Part A 111 (2018) 73-82. https://doi.org/10.1016/j.compositesa.2018.05.022

[6] R. Xu et al., Balanced strength and ductility in CNT/Al composites achieved by flake powder metallurgy via shift-speed ball milling, Composites Part A 96 (2017) 57-66. https://doi.org/10.1016/j.compositesa.2017.02.017

[7] H. Zhang et al., Enhanced mechanical properties of Al5083 alloy with graphene nanoplates prepared by ball milling and hot extrusion, Mat. Sci. & Eng. A 658 (2016) 8-15. http://dx.doi.org/10.1016/j.msea.2016.01.076

[8] Zheng Zhong et al., High-content graphene nanoplatelet reinforced aluminum composites produced by ball milling and hot extrusion, Science China Technological Sciences 63 (2020) 1426-1435. https://doi.org/10.1007/s11431-020-1670-4

[9] M. Negendank et al., Extrusion and characterization of aluminum/graphene composites, Proceedings of the 24th Int. Conf. on Material Forming (2021). https://doi.org/10.25518/esaform21.3714