COB-2023-1525
ADDITIVE MANUFACTURING OF COPPER-GRAPHENE COMPOSITES BY 3D-EXTRUSION

Milene Follmann
Camila Gonçalves
Manuela Furlani da Silva Soares
Natália de Freitas Daudt
Materials Technology and Mechanics Group (GMAT-UFSM), Federal University of Santa Maria, 97105900, Brazil
milene.follmann@acad.ufsm.br, manuela-furlani.soares@acad.ufsm.br, camila.goncalves@acad.ufsm.br, natalia.daudt@ufsm.br

Abstract.
Additive manufacturing (AM) is an attractive route for manufacturing copper components with complex shapes. Therefore, the goal of this study was to investigate the viability of the 3D extrusion of graphene-reinforced copper composites. Samples were printed in a house-customized 3D extrusion printer. For preliminary tests, pastes with an aqueous solution of carboxymethylcellulose were produced and cold pressed, going through debinding and sintering in a vacuum furnace. These samples were characterized regarding their microstructure by optical and scanning electron microscopy, porosity by Archimedes density method, and mechanical properties by microhardness and compression tests. Graphene addition tends to promote sample strengthing and increase porosity, which has the opposite effect on the mechanical properties. *Analyzing the results, samples containing 0,5% graphene, stood out for their low porosity, higher hardness, and compression strength. Due to its properties, this could be a good composition for printing.*

Keywords: 3D extrusion, Nanocomposites, Additive Manufacture, Copper-graphene, Copper

1. INTRODUCTION

Additive Manufacturing (AM) is a revolutionary technology that allows the production of high-precision and complex components, utilizing layer-by-layer deposition. Copper is widely used in the industry due to its physical and chemical properties, like high electrical and thermal conductivity, corrosion resistance, and conformability. AM can enable the production of complex-shaped copper for lightweight heat exchangers. However, mechanical properties such as stiffness, strength, and hardness of pure copper present a challenge for some applications, such as aerospace and automotive industries. Adding alloying elements to copper can increase the mechanical properties, however, it deteriorates the thermal and electrical conductivity.

The addition of graphene is a possible solution to the problem due to its electrical properties, hardness, and low density, the nanomaterial can increase the mechanical properties with a minimal effect on the copper conductivity (Pavithra, C.L. 2014). Copper-graphene composites have the potential to achieve the required overall properties, becoming an interesting material for additive manufacturing. A number of important studies have significantly advanced the field of additive manufacturing extrusion of copper-graphene composites, demonstrating methods for mixing graphene and copper efficiently, maintaining good mechanical and thermal properties. AM is an attractive route for the production of graphene-reinforced copper composites. 3D extrusion, which has been under development for pure copper production (Signor, F. 2023), can be applied for low-cost production of complex-shaped graphene copper composites. Therefore, in this study, the effect of graphene addition on copper pastes used for 3D extrusion was investigated.

2. MATERIALS AND METHODS

2.1 Materials

The starting materials for this study were Carboxymethylcellulose Powder (CMC) purchased from LabSynth (Batch 218137), distilled water, graphene nanoplatelets (GNPs) purchased from AlphaAeser (Batch T07H030), and Electrolytic Copper Powder by Dinâmica with purity of 99,9% (Batch 122780).

2.2 Paste Production and Cold Compaction

Initially, it was produced an aqueous solution of CMC in a mass proportion of 99/1. After the addition of the polymeric powder to the distilled water, the solution was heated up to 80 ºC under a magnetic stirrer until it was completely diluted.

After that, nanopellets of graphene were weighed and then a quantity of binder was added, the proportions used are described in Table 1. These materials were mixed to avoid graphene agglomeration in the samples. Lastly, the previously weighed copper powder was added to the paste and mechanically mixed.

The materials were weighed on a scale with 0,001g of precision. Group 88Cu, composed of pure copper, was used as a reference sample. As the ratio of graphene increases, the difficulty of distributing the nanoparticles homogeneously through the mix increases, for this reason, this powder was mixed first with the binder and only after the copper was added. The groups were classified according to their composition.

Table 1. Samples composition and processing parameters.

Group	Powder Load Composition (wt.%)	Powder loading (wt.%)	Sintering Temperature (ºC)
88Cu	100 Pure Copper	88	880
88Cu0.5Graf	99.5 Copper + 0.5 Graphene	88	880
85Cu1.0Graf	99.0 Copper + 1.0 Graphene	85	930
80Cu0.5Graf	99.5 Copper + 0.5 Graphene	80	980
80Cu3.0Graf	97.0 Copper + 3.0 Graphene	80	930
77Cu3.0Graf	97.0 Copper + 3.0 Graphene	77	930

The method of production consists of the deposition of the metallic pastes in a cylindric mold with an inner diameter of 10 mm and then compacting it at 50 MPa, resulting in green samples, as shown in Figure 1. All the green parts were weighed on a scale with 0,001 g of precision and had the length measured with a caliper with 0,05 mm of precision, these collected data enabled the calculation of the volume and density of the respective samples.
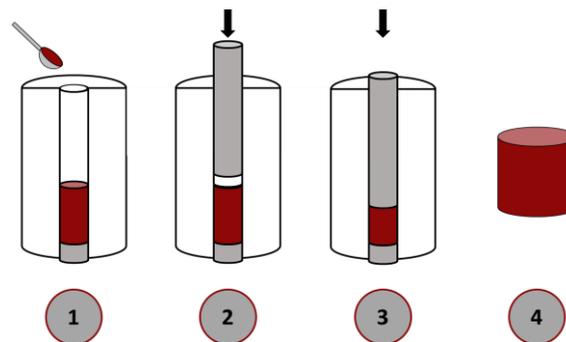

Figure 1. Process of Compacting Pastes into Green Pieces

This technique allows a wide range of viscosity, but it was noted that with the carboxymethylcellulose binder, the material extruded from the mold during compaction was homogeneous, indicating adherence of the powder in the viscous binder. It's important to recognize the effect the proportion of graphene causes in the green samples. Group 88Cu0.5Graf did not present sufficient mechanical stability, it had fissures and broke after demolding, evidencing an inadequate composition, but when the percentage of binder added was increased (Group 80Cu3.0Graf and 77Cu3.0Graf) there weren't any visual cracks in the structure.

2.3 **Debinding and Sintering**

Thermal treatment was conducted in a tubular furnace under a vacuum. The green samples were placed in a crucible with a thermocouple. Primarily, for the debinding, the heating rate was kept 2ºC/min until it reached 500ºC, remaining 30 minutes at this temperature to complete the process of removal of the polymeric binder. Then, once this part of the process was concluded, the heating rate was increased to 10ºC/min until it reached the sintering temperature, which provides sufficient energy to promote diffusion and densification, this temperature was kept constant for 120 minutes. The sintering temperature for each sample group is listed in Table 1. In the end, the pieces were slowly cooled inside the furnace until they were at room temperature.

Group 80Cu3.0Graf presented fissures and broke after sintering, evidencing an inadequate composition, but when the percentage of binder was increased to 23% for the same percentage of graphene, the pieces exhibited sufficient mechanical stability.

The volumetric retraction and densification of the samples are a consequence of the sintering process, due to neck formation, a significant quantity of pores closes. Again, the mass, length, and diameter were measured with a caliper with 0,05 mm of precision, obtaining volume and density.

3. 3D EXTRUSION

The 3D printer used in this study is a Duraprinter from the C series, model C01.The motor rotates a helix that extrudes the paste according to the CAD previously made. The nozzle moves along the X, Y, and Z axis, being able to produce three-dimensional pieces and it has an inner diameter of 3 mm. The printing parameters were adjusted in the Software Ultimaker Cura, the filling pattern chosen was 100% and the printer operated at room temperature. The velocity of the extrusion was 33.3 mm/s and the velocity of the nozzle was set to 3.33 mm/s. The geometry chosen for printability tests was a cylindrical piece of 25,4 mm in diameter and 5mm in height.

Analyzing the previous results and compatibility with the printer model, the chosen binder was a solution of carboxymethyl cellulose due to its higher capacity of maintaining one phase with the copper-graphene powder. Therefore, to magnify this effect, the percentage of carboxymethyl cellulose was increased to 2% in the solution. Firstly, the printability of pure copper was tested, it was possible to print a paste composed of 60% of pure copper and 40% of binder. The samples were sintered at 930°C.

Due to the results of compaction tests, it is possible to assert that the composition with the most interesting properties was group 80Cu0.5Graf. It had the best resistance to micro indentation, best performance in compression, and lowest apparent porosity, and the percentages of volumetric retraction and densification were befitting. For printing copper with 0.5% graphene it was necessary to prepare a paste of proportion 60/40 of powder/binder and position it inside a cylinder with a piston, as shown in the figure below. This composition is still being analyzed.

Figure 2. Schematic representation of printing copper-graphene composites by 3D-Extrusion and composites pieces printed

3.1 Metallographic Preparation

Some of the sintered samples underwent metallographic preparation to be used in other tests, like microhardness and optic microscopy visualization tests. The pieces for microscopy were cut perpendicularly to the symmetry axis to avoid surface defects. For that, the cross-section of the samples was prepared by cutting with. The machine used was a precision cutter with the diamond disk at 125rpm, under water cooling with water contact to reduce abrasiveness in the pieces. Afterward, the samples were embedded in Bakelite to facilitate the next process. The samples were sanded and grided with water sandpaper with granulometry 200, 400, 600, and 1200. Then, polishing was performed on a metallographic polisher at 600 rpm with a fabric disc until there were no more scratches when visualized through an optic microscope.

3.2 Sample Characterization

The Hardness of the samples was measured using a Vickers Microhardness tester (Shimadzu, Japan). Ten measures were conducted in each sample using a load of 980 mN for 15 s. The compressive strength of the samples was measured using a uniaxial compression test on a universal testing machine (EMIC 1000). For this test, the samples were lubricated with graphite, which reduces the effect of friction, reducing the unwanted effect of embrittlement. The parameters adopted as standard for this test were 0.02 mm/s for the compression speed and 70 kN was chosen as the closing load for the test.

Optic microscopy is an important tool to observe characteristics of the microstructure, the equipment utilized for the test is a Zeiss which, due to the properties of the metallic materials, uses the method of light reflection. Pictures of each group of samples were taken after the metallographic preparation, and a digital camera with a resolution of 16 megapixels and an optical zoom of 5x was attached to the microscope. The objective lenses used were 2.5x, 5x, 10x, 20x, 50x and 100x.

The X-ray diffraction was performed in a Brucker D8 Advance configured in Bragg-Brentano geometry with a tungsten filament. The source is a tube with a copper anode. The equipment operated at a power of 1.6kW (voltage of 40

kV and current of 40 mA) and a sweep was conducted from 6° to 80°. The parameters used were a step size of 0.02° at a scanning speed of 1.5 s.

4. RESULTS AND DISCUSSIONS

According to Table 3, analyzing the microhardness, group 80Cu0.5Graf had the highest hardness and 77Cu3.0Graf had the lowest, which indicates that increasing graphene amount to values higher than 0.5% leads to a decrease in hardness. This hardness decrease may be related to the high porosity. It is interesting to notice that 85Cu1.0Graf and 80Cu0.5Graf values were higher than 88Cu, the reference group, demonstrating an improvement of hardness with the graphene addition.

Table 2. Volume Retraction, Densification, Apparent Porosity and MicroHardness of sintered samples

Group	Volumetric Retraction (vol%)	Apparent Porosity (vol.%)	Microhardness (HV)
88Cu	15.6 ± 1,4	9.27 ± 0.43	34.0 ± 3.4
80Cu0.5Graf	19.2± 0,6	6.16 ± 1.62	46.01 ± 9.4
85Cu1.0Graf	10.7 ± 0,4	13.46 ± 0.02	40.9 ± 10,9
80Cu3.0Graf	4.9 ± 1,9	25.39 ± 0.60	*
77Cu3.0Graf	9.7 ± 0,0	18.64 ± 0.00	26.1 ± 7.7

*Couldn't be measured

Group 80Cu0.5Graf had the largest volume retraction and densification. Groups 85Cu1.0Graf, 80Cu3.0Graf, and 77Cu3.0Graf had volumetric retraction below 11% and porosity higher than 10%, which indicates increasing graphene % leads to higher porosity.

The graphene addition seems to lead to two main effects: improved strengthening and porosity. These two effects have oppositive impacts on the mechanical properties. At small graphene addition, the strengthening had a main role so that hardness increases, while at higher graphene amounts the effect of porosity is more pronounced and the samples have a lower hardness. Sintering paraments and graphene dispersion require further optimization in order to decrease porosity and improve the mechanical properties of graphene-reinforced copper composites.

Light microscopy images indicate that pores are well distributed in the samples, however, there are some large pores. Figure 3a) is from 80Cu0.5Graf and 3b) is from 77Cu3.0Graf. Both of them have a significant quantity of pores, but the one with 3% graphene has more, indicating that the addition of graphene increases porosity.
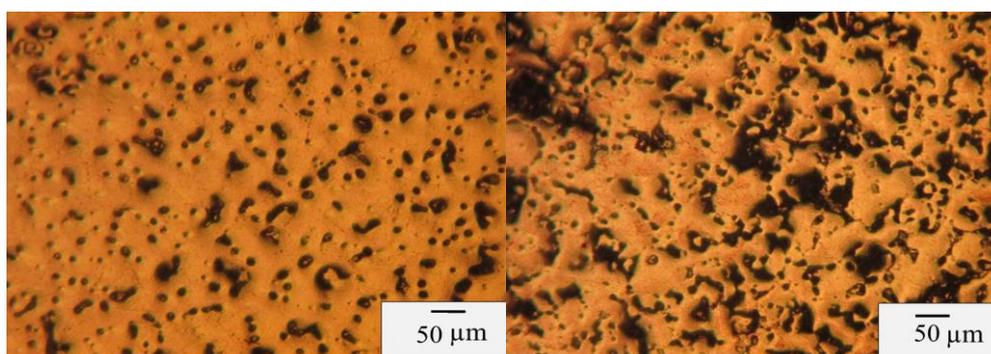

Figure 3. Microphotography of polished sample number 3 of 80Cu0.5Graf (a) and number 2 of 77Cu3.0Graf (b)

Analyzing the compression curves in Figure 4, it is possible to notice that samples without and with 0.5 % of graphene have similar behavior and present a higher ductility, 88Cu samples show a slightly higher yield strength. The graphene addition in higher amounts of 1% and 3% considerably decreases yield and compression strength, so the sample with 3% graphene has the lowest performance, which is related to the higher porosity of these samples as discussed above.
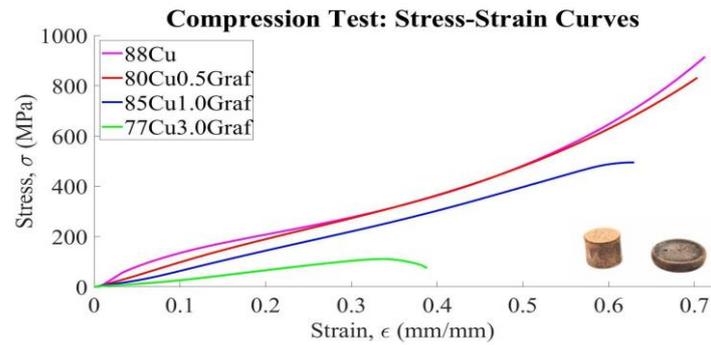
Figure 4. Compression Test: Stress-Strain Curves

In all analyses, it was possible to identify only the peaks related to the face-centered cubic crystal structure of pure copper. The peak located at $2\theta = 43.317$ was in the direction [1 1 1] of the crystal system, the unit cell dimension in this direction is 2.08712Å. The peak located at 50.449° represents the direction of [2 0 0] and the cubic unit cell has a size of 1.80750 Å. Lastly, the peak in 74.126° is in the direction [2 2 0] and has a side of 1.27810 Å. There was no observed peak related to carbides, graphene, or graphene oxide phases, which suggested that the graphene is homogenously distributed in the metal matrix. The results of the X-ray diffraction demonstrated satisfactory because there are only Cubir Copper phases, while graphene acts as an interstitial element, which doesn´t form its own phase.
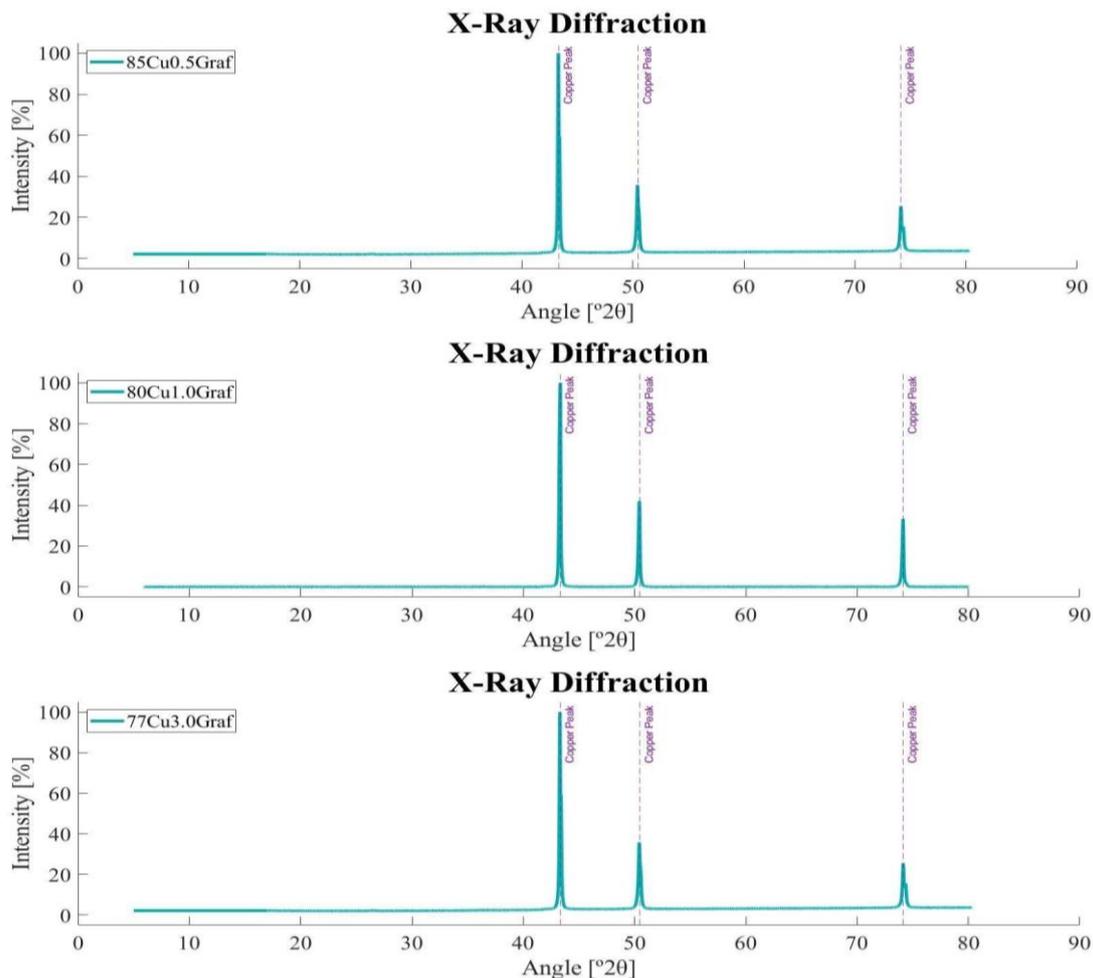

Figure 5. X-Ray Diffraction Tests

Pure copper was successfully 3D printed in a proportion of 60 wt.% of powder load and 40wt.% of the binder, the sintering temperature chosen was 980°C and the programming was the same as the compacted samples. The pieces

presented a linear retraction in their diameters of 19.17% ± 3.23%, which indicates a proper thermal treatment. The porosity measured by image analysis of SEM images indicated a porosity of 1.43 ± 1.22, lower than all the compacted samples. Moreover, the Vickers Microhardness test resulted in 96.67 ± 5.84 HV, around double the value of the compacted ones. The preliminary 3D printing experiments revealed that was possible to print copper-graphene composites.

Copper-graphene composites were also successfully printed using a paste with 60 wt.% powder load. During the printing process, it was possible to observe that the amount of binder can be reduced because the paste presented low viscosity. The sintering experiments for this composition are currently under investigation and, later on, the viscosity of the composite will be studied and analyzed, with the intent of printing complex-shaped pieces.

5. CONCLUSION

The findings reveal that as the percentage of graphene increases in the composites, microhardness tends to decrease. Porosity also increases with higher graphene content. The results obtained so far demonstrate that is possible to produce copper-graphene composites from 3D extrusion pastes. Graphene addition affects the paste rheology, changing the sample stability in the green state, more tests are currently under investigation to determine the graphene effect in the green samples.

Graphene addition tends to promote sample strengthing and increase porosity, which has the opposite effect on the mechanical properties. At low graphene amounts, strengthening can be noticed by improvement of microhardness, at higher graphene amounts porosity plays a major role, and microhardness and compression strength are reduced. However, it is expected that porosity can be decreased by optimization of sintering parameters, which could result in higher mechanical properties. Overall, the research highlights the potential of copper-graphene composites for additive manufacturing and underscores the importance of continued exploration and development in this field to unlock their full range of applications in various industries.

6. ACKNOWLEDGEMENTS

7. REFERENCES

Jiang, Q., Zhang P., Yu, Z., Shi, H., Wu, D., Yan H., Ye, X., Lu Q ., Tian, y., 2021. "A Review on Additive Manufacturing of Pure Copper". Coatings, vol. 11(6), p. 740.

ISO/ASTM52900-15, 2015. "Standard terminology for additive manufacturing—general principles—terminology". ASTM International, West Conshohocken, PA.

Pavithra, C., Sarada, B., Rajulapati, K., Rajulapati K., Rao N., Sundararajan G., 2014. "A New Electrochemical Approach for the Synthesis of Copper-Graphene Nanocomposite Foils with High Hardness". Sci Rep 4, Article n. 4049.

Signor, F., Bevilaqua, W., Caravalho, M.J., Pozzebon, A.B., Limberger, I., Daudt N.F. "Fabrication of copper parts by 3D Extrusion of highly viscous paste", *In proceedings of the EuroPM 2023*.Lisbon, Portugal.

8. RESPONSIBILITY NOTICE

The authors are the only ones responsible for the printed material included in this paper.