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Use of Graphene for Shaped Charge Liner Materials

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Abstract. The paper presents some selected results of tests performed as part of a research task titled "Use of graphene and new multilayer explosive material technologies in shaped charge liner materials". The main aim of the experiments was to test the possibilities of using graphene as an addition to materials used for shaped charge liner production. The primary factors that need to be considered when selecting materials for shaped charge liners are presented. The paper contains a description of the powder materials used, as well as a description of the primary manufacturing steps, encompassing the powder blend preparation, pressing and sintering operations. The results of experiments intended to determine the effects of selected manufacturing process parameters on the porosity of the resulting compacts and sinters are shown, both for products made of pure copper powder and graphene-coated powder. Subsequently, test results for manufacturing of liners made using copper powder pressed using the die and isostatic methods are presented. Liners made of copper powder blends with a varying content of graphene-coated copper powder were also manufactured, and densities and porosities of the resulting sinters were compared.
Keywords: powder metallurgy, shaped charge liner, graphene

1. INTRODUCTION

Shaped charge systems have been widely utilised in armaments for many years. They are applied as payload in missiles and torpedoes, anti-tank artillery shells, grenades and mines. Shaped charge effectiveness is expressed as the ratio of resulting crater depth to explosive charge diameter [1].

During the early period of shaped charge technology development, the effectiveness of the shaped charges was not high, but it enabled the destruction of or damage to the armoured targets then in use. Due to the limited knowledge base, little attention was paid during that time to important engineering, technology and material details in shaped charges, e.g. selection of the right materials for liners. Only the development of techniques that enabled the process of shaped jet formation to be observed, especially the X-ray-based methods of recording rapidly occurring phenomena [2-3], as well as photographic methods [4], allowed basic quantitative and qualitative relations to be formulated, and engineering and process requirements of shaped charge systems to be determined. Conclusions from these studies were further expanded and verified after computer simulations became commonplace [5-9]. These resulted in the creation of highly effective shaped charge systems, enabling penetration of armour layers of a thickness exceeding 6÷8 diameters of the charge used.

A significant number of publications on theoretical works and experimental tests concerning shaped charges enables the determination of the primary factors affecting their effectiveness. With these as a basis, it can be stated that penetration depth is affected by three main factors [10, 11]:

1. The system engineering solution.
2. The explosive charge type and charge loading method.
3. The liner material and manufacturing technology.

The last of these factors was the subject of the study described in this paper. The right shaped charge effectiveness is achieved by using liners made of materials ensuring formation of a jet with a long continuous section, high front velocity, density and a long period of initial fragmentation [14].

During jet formation, liner material is subjected to extreme accelerations and deformations. It is estimated that pressure affecting the side surface of the liner reaches 20÷40 GPa, while relative deformation of the material is approximately 1000% at deformation speed $10^5 s^{-1}$ [13]. Based on experimental tests it can be assumed that the temperature of the material under deformation does not exceed 600÷700 K and as has been ascertained [14], it is the result of an increase in internal energy of the material due to its compression and internal friction caused by plastic deformation [15]. Individual jet fragments move at different speeds, with the front travelling at a speed of approx. 8÷10 km/s, and its end – at a speed of approx. 2 km/s.

Given the information above, the basic factors to be considered when selecting liner materials can be determined:

- density,
- melting point,
- sound propagation speed,
- strength and plasticity.

A material commonly used for shaped charge liners is copper. The use of this material results from its good plastic properties (longitudinal elongation during static tests is approx. 50%), which enable the formation of a jet of a regular shape and the right length. The melting point of copper is 1356 K, almost twice the temperature reached by jet material under deformation, which – being a solid when moving through the air – is not scattered as a result of the aerodynamic interactions with the medium and maintains its shape and cohesion. Furthermore, copper recrystallisation initiation temperature is 473 K and is lower than the temperature of the jet. This creates the possibility of dynamic recrystallisation occurring during jet formation [16].

In the experiments presented later in this paper, copper powder coated with graphene was used as the material for shaped charge liner manufacturing.

Graphene is an allotropic form of carbon, creating a flat structure composed of carbon atoms, and as it has a thickness of one atom, by way of a simplification it is considered a two-dimensional structure. Graphene has attracted the attention of industry due to its specific properties, especially electrical, optical and mechanical ones [17].

Experimental results indicate that the addition of graphene to metals (e.g. copper) significantly affects their strength properties [18-20].

The main aim of the study was to determine the possibilities of using graphene as an addition to materials that can be used to manufacture elements (liners) of shaped charge systems, which would enable the production of such systems for use, for example, in 40 mm grenade launchers. The individual steps of the shaped charge element production process were verified.

As part of the study, comprehensive tests related to selection of engineering parameters and optimisation of the production process of liners made both of copper-graphene composites and without graphene addition were conducted. This optimisation was intended to provide a material with the right density and good mechanical properties. This required tests of mechanical parameters, as well as optical microscopy (qualitative and quantitative) and electron scanning microscopy structural tests to be performed.

Below, the results of a study conducted at the Institute of Armament Technology of the Faculty of Mechatronics and Aerospace of the Military University of Technology (Warsaw, Poland), which concerned the possibilities of using graphene additions to materials for sintered shaped charge liners.

The study utilised copper powder coated with graphene, produced by the Institute of Precision Mechanics (IPM) in Warsaw (Poland). The technology of producing this material is protected by the patent no. PAT.225890 titled „Sposób wytwarzania struktur węglowych zawierających grafen na proszkach miedzi z wykorzystaniem obróbki cieplno-chemicznej" ("A method of producing carbon structures containing graphene on copper powders using thermal and chemical treatment") dated 1 December 2016.

2. PREPARATION OF SAMPLES FOR TESTS

The following powders or powder blends were used to prepare samples:

a) copper powder with a dendritic grain shape (electrolytic) and grain size 40-63 μm,
b) electrolytic copper powder with grain size 40-63 μm and covered with graphene, produced in the IPM (CuG),
c) copper powder with a spherical grain shape (atomised) and grain size 40-63 μm,
d) blends of graphene-coated powder and copper powder in various proportions.

The production process comprised the following operations:

1. Preparation of powder blends.
2. Preparation of compacts.
3. Sintering processes.
4. End treatments of sinters.

The specific properties of input powders have a significant impact on the selection of equipment and powder blend production conditions.

Powder blends, i.e. copper + graphene-coated copper were prepared in a blade mixer. The mixing duration (1 hour) and mixer rotation rate were adjusted so that complete homogenisation of the chemical composition and grain size distribution of the blends could be achieved. It was found that longer mixing durations do not lead to significant changes in the properties of the resulting blends and have no economic justification.

Test samples were pressed using two methods: die pressing and cold isostatic pressing (CIP). The CIP pressure was within the 250-300 MPa range, and the duration for which flexible moulds filled with powder blends were maintained under the given pressure was 2 to 5 minutes. The press decompression from the adopted pressing pressure to atmospheric pressure was conducted gradually so as not to cause compact cracking.

During the testing programme, two processes of compact sintering were used: in a dissociated ammonia atmosphere and vacuum sintering.

The first sintering process was conducted in a tubular furnace in an atmosphere of dissociated ammonia at the dew point of -20°C. Because oxide layer reduction on the surface of metallic powder grains and oxide reduction inside the powder grains should occur during pre-sintering, the temperature range adopted must ensure that all reactions related to these temperatures can be completed.

For this reason, a temperature hold had to be used during the sintering process, which ensured complete reduction of oxides. It was assumed that this stage of sintering should be executed at the following parameters: temperature 350°C, duration 1 hour, while sintering proper was conducted at a temperature of 920°C and for a duration of 1 hour.

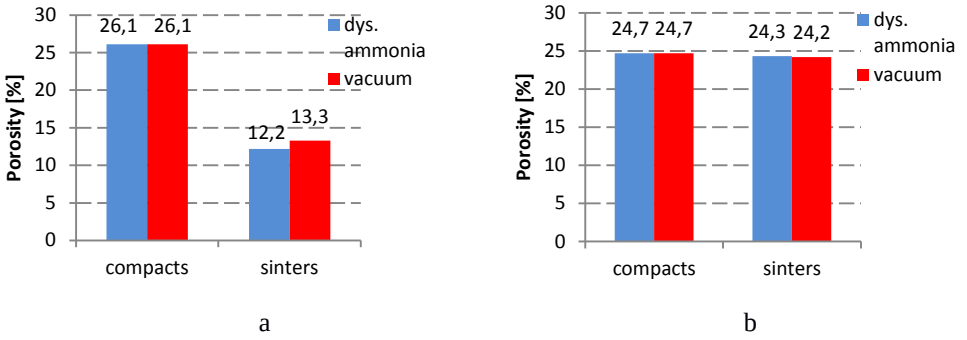
For sintering in a dissociated ammonia atmosphere, an important condition is to provide constant flow of the dissociated ammonia atmosphere or hydrogen atmosphere of the right volume through the furnace, during the entire sintering process. The atmosphere volume is usually adjusted depending on the size of the charge and furnace structure. A flow equal to 15 volumes of the furnace chamber during 1 hour was applied.

During the tests, the other proper sintering method was used as well – vacuum sintering. This should enable the acceleration of the sinter consolidation process, with concurrent dissociation of copper oxides and removal of hydrogen residue left after the first sintering stage. Subsequently, the samples were subjected to machining.

3. TEST RESULTS

During the first stage, comprehensive tests of the powders and samples sintered according to the methodology described in section 2 were conducted. The properties of the test powders were determined, e.g. bulk density, tap density, grain size distribution. Subsequently, cylinder sample tests were performed (density, porosity, selected mechanical properties). The results enabled the optimisation of the production process of sinters with the assumed chemical composition. A separate group of tests were experiments concerning the production of sintered liners. In this case, density and porosity (including porosity distribution) of sinters for different variants of the manufacturing process were determined. Below, selected example results of the tests are shown.

Results of porosity tests of die pressed samples and sintered using copper powder and graphene-coated copper powder are shown in Figure 1.



a b

Fig. 1. Effects of the protective atmosphere utilised on the density of compacts and sinters: a – electrolytic powder, b – graphene-coated electrolytic powder

Based on the charts shown, it can be concluded that for sinters made of copper powder, slightly better results were achieved with the use of sintering in NH_3. On the other hand, it was observed that sinter consolidation occurred for neither atmosphere when sintering graphene-coated powders (only a minor reduction in porosity occurred). For this reason, it was decided that in the next phase of the study, only blends of copper powder with graphene-coated copper powder (in various proportions) would be used for experiments.

Additionally, microstructure tests of sinters made of CuG powders revealed the presence of large SiC inclusions (Fig. 2), which could lead to a deterioration in plasticity of these materials.

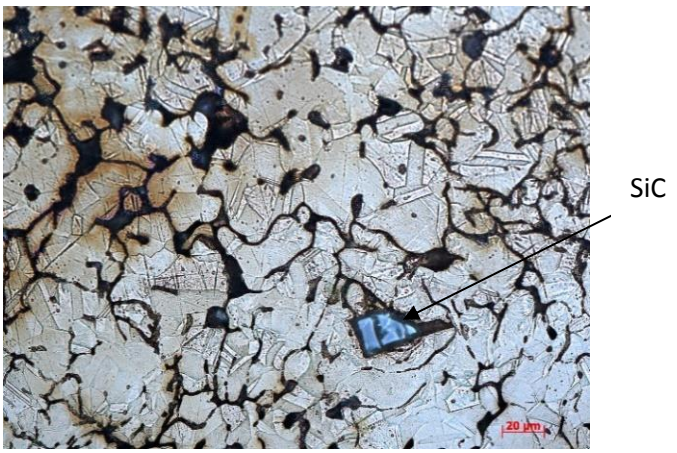


Fig. 2. Microstructure of a sinter made of a graphene-coated powder (zoom 1000x)

Silicon carbide is used during the process of coating powder grains with graphene. Currently, studies on eliminating this impurity are in progress at the IPM.

Sintering tests of die-pressed spherical powders demonstrated that the resulting materials are characterised by very high porosity (Fig. 3).

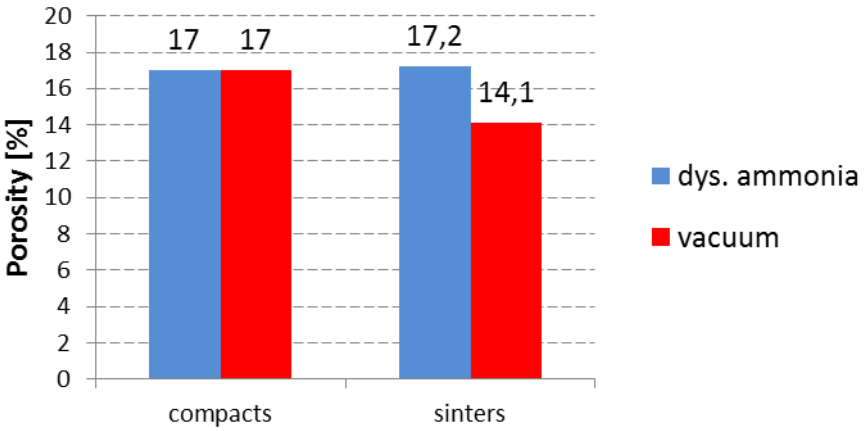


Fig. 3. Effects of the protective atmosphere utilised on the density of compacts and sinters made of spherical powder

The use of vacuum sintering in this case enabled the achievement of a somewhat better result, although still inferior to the use of electrolytic powders, and for this reason it was decided to exclude the first material from further tests.

As a result of further tests of cylindrical samples made of graphene-coated Cu powder and of blends of this powder with Cu powder, it was found that increasing the content of the former increased sinter porosity. For this reason, powder blends with a CuG content no greater than 20% were used in subsequent tests.

During the next stage of the study, tests of production of the sintered semi-fabricated element for liners were conducted. During the first phase, liners made of copper powder (without CuG powder addition) with dimensions similar to liners used in GNPO grenades were manufactured. Two pressing methods were utilised: die and cold isostatic (CIP). In the first case, the compact wall thickness was 1.3-1.7 mm, in the second case – 5-7 mm. For die pressing, the pressing pressure was assumed to be the ratio of punch pressure to liner base diameter. Table 1 shows the test results.

For die-pressed sinters, the highest sinter density (8.14 g/cm^3) was achieved with the use of 98 MPa pressure. On the other hand, for sinters obtained using the CIP method, the highest sinter density (8.61 g/cm^3) was achieved with the use of 300 MPa pressure. These parameters were assumed for further tests.

For die-pressed liners, liner walls had a thickness twice the thickness of the intended liner wall (GNPO grenade). For this reason, there is a possibility of achieving a higher liner density once sinter wall thickness is reduced.

Table 1. Results of density and porosity tests of compacts and sintered liners

			Compacts		Sinters	
Material	Pressing method	Pressure [MPa]	Density [g/cm^3]	Porosity [%]	Density [g/cm^3]	Porosity [%]
Cu	die	74	4.77	46.8	7.25	19.1
Cu	die	98	5.03	43.9	8.14	9.2
Cu	die	123	5.31	40.7	8.05	10.2
Cu	die	147	5.2	42.0	7.94	11.4
Cu	CIP	100	3.7	58.7	5.58	37.7
Cu	CIP	150	6.12	31.7	8.05	10.2
Cu	CIP	200	6.49	27.6	8.52	4.9
Cu	CIP	250	6.83	23.8	8.49	5.2
Cu	CIP	300	7.09	20.9	8.61	3.9

Subsequently, possibilities of obtaining sintered semi-fabricated elements for producing liners from CuG+Cu blends were investigated.

In accordance with the arrangements made with the Institute of Precision Mechanics, the following sample variants were prepared:

– liners made of Cu powder,
– liners made of 1%CuG + 99%Cu powder blend,
– liners made of 5%CuG + 95%Cu powder blend,
– liners made of 10%CuG + 90%Cu powder blend.

Additionally, liners made of 10%CuG + 89%Cu+1%Kenolube (lubricant – zinc stearate) powder blend were sintered. Liners were pressed using the die method. Liners manufactured according to the first variant were handed over to the IPM for graphene coating. In this case, the intention was to perform tests related to the selection of the parameters for coating the surfaces of such elements with graphene. Table 2 shows the results of the liner density and porosity tests.

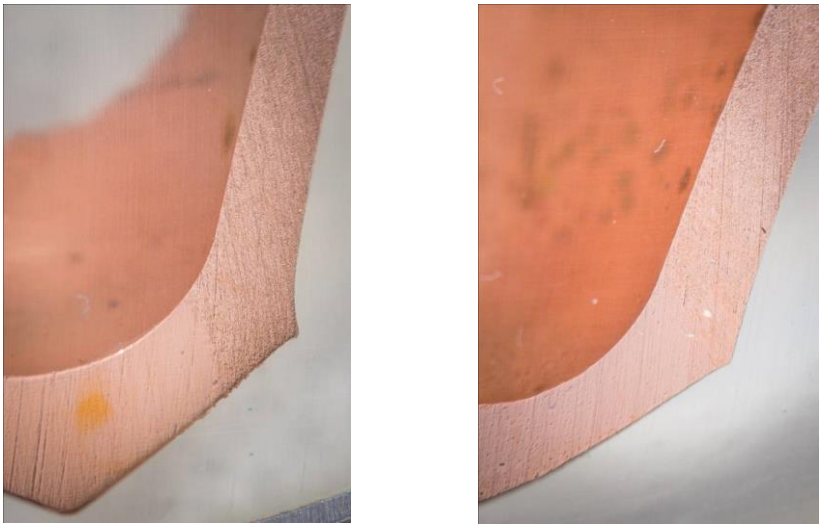
The results indicate that the use of die pressing can produce sinters, serving as semi-fabricated elements for the production of shaped charge liners, with a porosity of 10.5%. As has been noted before, it is likely that by reducing wall thickness, sinters with lower porosity can be obtained. Increasing the content of graphene-coated powder resulted in reducing sinter porosity, although the reduction was no greater than 1%.

Adding the lubricant Kenolube led to only a minor reduction in sinter density, while increasing compact strength (including damage resistance) and facilitating the process of removing compacts from the die.

Table 2. Results of density and porosity tests of compacts and sintered liners

Material	Pressing method	Pressing pressure [MPa]	Density [g/cm^3]	Porosity [%]
Cu	die	98	8.11	9.5
99Cu+1CuG	die	98	8.02	10.5
95Cu+5CuG	die	98	8.07	9.9
90Cu+10CuG	die	98	8.11	9.5
89Cu+10CuG + 1Kenelube	die	98	8.01	10.5

Tests of porosity distribution in die pressed liners were also carried out. Due to the friction occurring between powder and die walls, it was expected that pore distribution in compacts, and consequently in sinters, would not be uniform. Sample images of test sinter profiles are shown in Figure 4.



a) b)

Fig. 4. Porosity distribution in die-pressed liners:
a – without lubricant, b – with lubricant

Areas of low porosity can be noted in the images shown, located close to the apex section of the liner, while on the side surface, the value of this parameter increases significantly. Such a distribution of pores is mainly the result of pressing machine design and of the pressing process.

For liners pressed without a lubricant being added, the edge of this area is clearly visible. For this reason, the design of the tools employed must be modified, in order to improve the properties of the sinters produced. A more uniform porosity distribution was achieved for samples made of powder blends with the lubricant added.

Yield strength of sinters made of blends with various chemical compositions was also determined. The results are shown Table 3.

Table 3. Sinter yield strength test results

Sample type	Yield strength [MPa]
Cu	79.4
95%Cu+5%CuG	86.0
90%Cu+10%CuG	88.1
89%Cu+10%CuG + 1%Kenolube	87.0
Cu surface coated with graphene	54.5
Cu subjected to thermal treatment	45.0

The addition of copper powder coated with graphene resulted in a slight increase in plasticity of the test sinters. Yield strength values for materials coated with a graphene layer were determined. In this case, a marked drop was observed in this parameter. This effect can be explained by the fact that during graphene coating, the samples were heated to a high temperature (approx. 1000°C), which caused grain expansion and consequently lowered the yield strength (described by the Hall-Petch relationship). This was confirmed by tests of samples that were subjected to the heat treatment process corresponding to that which accompanies the graphene coating operation. For the subsequent part of the study, preparation of samples for tensile strength tests is envisioned, which will enable determining the plasticity of the sinters tested.

4. CONCLUSIONS

The tests conducted to date indicate that trial sintering of powders not coated with graphene enabled the production of sinters with a relatively high density. In this case, better results were achieved with the use of electrolytic powders. Sintering in dissociated NH_3 yielded similar results to sintering in vacuum. It was ascertained that the use of the sintering parameters adopted (920°C, 1h) enables the production of sinters of the required density.

Isostatic pressing enables the production of sinters of a higher density than die-pressed materials (by more than 8% for the best results). However, the latter is more suitable for mass production (due to higher throughput and the possibility of automation), and for this reason, the process should be modified by changing the design of the tool set to achieve greater density of compacts.

The use of graphene-coated powder as the main sinter ingredient did not yield positive results. Such materials were characterised by very poor properties (porosity greater than 24%), and consequently in subsequent experiments, blends with a lower content of graphene-coated powder were used (up to 10% m/m).

Further tests will be aimed at obtaining sinters with CuG addition that possess a porosity consistent with the requirements for shaped charge liner materials (below 8%).

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Zastosowanie grafenu w materiałach na wkładki kumulacyjne

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Streszczenie. W artykule zaprezentowano wybrane wyniki badań przeprowadzonych w ramach realizacji pracy badawczej pod tytułem „Zastosowanie grafenu i nowych technologii wielowarstwowych materiałów wybuchowych w materiałach na wkładki kumulacyjne". Głównym celem wykonanych eksperymentów było zbadanie możliwości wykorzystania grafenu jako dodatku do materiału wykorzystywanego do produkcji wkładek kumulacyjnych. Przedstawiono najważniejsze czynniki, które należy wziąć pod uwagę przy doborze materiału na wkładki kumulacyjne. W artykule opisano zastosowane materiały proszkowe, jak również podstawowe etapy procesu wytwarzania, obejmujące operacje przygotowania mieszanki proszkowej, prasowania i spiekania. Zamieszczono wyniki eksperymentów dotyczących określenia wpływu wybranych parametrów procesu wytwarzania na porowatość otrzymanych wyprasek i spieków, zarówno produktów wykonanych z czystego proszku miedzi, jak i z proszku pokrytego grafenem. Dalej przedstawiono wyniki prób wytwarzania wkładek kumulacyjnych z użyciem proszku miedzi prasowanego metodą matrycową i izostatyczną. Wykonano również wkładki kumulacyjne z mieszanek z proszkiem miedzi z różną zawartością proszku miedzi pokrytego grafenem i dokonano porównania gęstości i porowatości otrzymanych spieków.
Słowa kluczowe: metalurgia proszków, wkładki kumulacyjne, grafen