Conditions for obtaining and characteristics of lead-free passive elements for high energy impact

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***Abstracts**: Compression was carried out of modified copper powder workpieces at a pre-determined value of the pressure. High temperature sintering of the workpieces in a neutral medium at a temperature of 1,000°C was performed. A high density metal-ceramic composite material was obtained. Its structure and physico-chemical parameters were determined. Lead-free prototypes were created, corresponding to the weight and dimensions of the reference standard lead passive elements for high energy impact.*
***KEYWORDS**: PRESSING, HIGH TEMPERATURE SINTERING, HIGH ENERGY IMPACT*

*1. **INTRODUCTION***

The use of lead in many products and devices such as piezoelectric elements, passive high energy impact elements and others poses certain risks to the human health and the environment. This calls for seeking alternatives and creating lead-free prototypes that perform the same functions. As of 1 June 2006, restrictions on the production and import of electronic components and other articles containing lead, as well as of equipment containing lead, have been introduced in the European Union. The requirements are set out in a series of EU documents (RoHS directives). In 2013, the Council of Ministers of the Republic of Bulgaria adopted a Decree on the conditions and procedure for equipment marketing in line with the restrictions on the use of certain hazardous substances (Decree of the Council of Ministers No 55/06.03.2013, published in the State Gazette No 24 of 12.03.2013).

According to the norms stated, as of 21.07.2016, no lead should be contained in ceramic, dielectric, metal-ceramic and composite materials which are part of integrated circuits, discrete semiconductors or high energy impact elements [1].

As is known, Directive 2017/2102 of the European Parliament and of the Council of 15.11.2017 amends Directive 2011/65/EU concerning the restriction of the use of certain hazardous substances.

Lead is prohibited in water pipes and as an additive in motor fuels and paints. It is also prohibited for use in hunting ammunition and as fishing tackle in most of Europe. The European Union with its Directive 2012/65/EU has also banned its use in balancing tires, as well as in electrical and electronic equipment.

Increasingly, regulatory burdens, processing costs and the costs of atmospheric discharges are also affecting the use of lead, including in the automotive, aerospace and nuclear energy industries and in consumer and sports goods, for medical purposes and more. [2, 3, 4, 5]

In the present study, experiments and studies have been carried out and a metal-ceramic composite has been created based on a modified copper powder, with a sediment composition of less than 100 microns, which complies with EC No 231-159-6. The chemical composition of the powder comprises the following chemical elements in weight %: Cu 99.5%; Ag 0.005%; Ag 0.005%; As 0.0002%; Fe 0.005%; Mn 0.002%; Pb 0.05%; Sb 0.005%; Sn 0.005%.

Workpieces were obtained whose density, hardness, microhardness, compressive strength and structure are equivalent to those of a standard lead sample. The new material from which the samples are made does not pose a toxic or environmental threat and can be successfully recycled after first use or at the end of the useful life of the product.

2. EXPERIMENTS

From the modified copper powder and using the powder metallurgy method, 10 pieces of sample bodies were compressed by bilateral pressing in a small matrix - Figure 1, [6].

***Figure 1**. Photo of the matrix for molding workpieces of passive elements*

The measured density ρ of 6 sample bodies is shown in Table 1, and a plot of the change in their density as a function of the applied force P is shown in Figure 2. Using the P - ρ curve of Figure 2, the optimal force P = 8,000 kg is determined, for which the density ρ corresponds to that of the reference lead samples.

***Table 1.** Density ρ of copper based sample bodies*

No	P [ton]	d [mm]	H [mm]	V [cm^3]	G [g]	ρ [g/cm^3]
1	2	10	14.40	1.13	6.88	6.08
2	4	10	11.30	0.89	6.30	7.10
3	6	10	10.50	0.82	6.40	7.77
4	8	10	11.00	0.86	6.90	7.98
5	9	10	9.98	0.80	6.40	8.17
6	11	10	9.80	0.77	6.50	8.15

These experimental results were preliminary, as changes in the samples were expected to occur at their high temperature sintering at 1,000°C, with a retention time of τ = 60 min. Indeed, the curve showing the dependence of the density after sintering ρ on the force P undergoes modification, as shown in Table 2 and Figure 3, and the compression pressure required for the final useful and correct density changes.

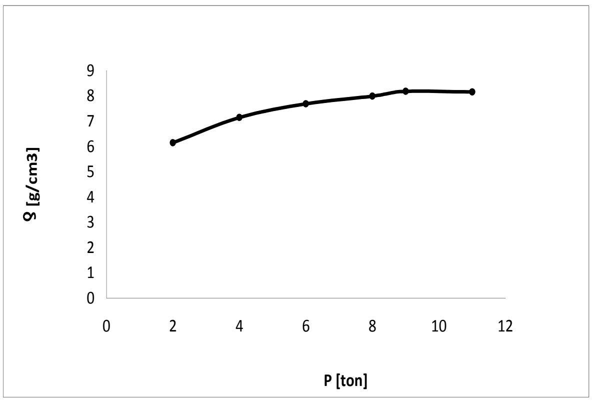


***Figure 2.** Dependence of the density ρ [g/cm^3] of copper based samples on the applied force P [ton]*

Figure 3 shows that a force of 5.5 tons must be applied to achieve a value of the density $\rho \approx 8$ g/cm^3 after sintering.

Table 2. *Density of copper based samples after heat treatment*

No	P [ton]	d [mm]	H[mm]	V [cm^3]	G [g]	ρ [g/cm^3]
1	2	9.0	13.00	0.82	6.70	8.11
2	4	9.8	11.60	0.77	6.20	8.05
3	6	10.2	12.60	1.03	6.50	6.50
4	8	10.3	12.98	1.08	6.70	6.20
5	9	10.0	13.20	1.03	6.30	6.11
6	11	10.28	12.0	1.00	6.50	6.53

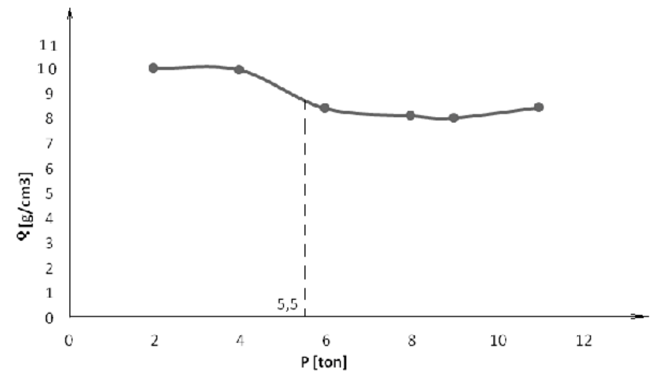


Figure 3. *Dependence of the density ρ [g/cm^3] of copper based samples on the applied force P [ton] after heat treatment*

10 workpieces were molded in working matrices with diameters roughly between 14.73 mm and 14.80 mm under the above mentioned conditions: force of 5.5 ton, sintering temperature of 1,000°C and isothermal retention time of 60 min. The parameters of the workpieces after pressing are shown in Table 3, and the parameters after high-temperature sintering are shown in Table 4.

Table 3. Density of copper specimens pressed with force P = 5.5 ton

No	P [ton]	d [mm]	H[mm]	V [cm^3]	G [g]	ρ [g/cm^3]
1	5.5	14.78	29.60	5.90	31.00	5.25
2	5.5	14.73	31.11	5.31	34.58	6.52
3	5.5	14.80	27.90	4.80	31.13	6.48
4	5.5	14.80	25.00	4.30	27.90	6.49
5	5.5	14.80	25.35	4.36	28.47	6.54
6	5.5	14.80	27.80	4.78	30.92	6.40
7	5.5	14.80	27.20	4.67	30.46	6.53
8	5.5	14.80	27.50	4.73	29.67	6.17
9	5.5	14.80	27.70	4.76	31.30	6.57
10	5.5	14.80	29.90	5.14	32.12	6.25

From the workpieces were produced 10 prototype samples of passive elements for high energy impact, equivalent not only in structure and physic-chemical properties, but also in size to the standard lead samples, as shown in Figure 4.

Table 4. *Density of copper based specimens pressed with force P = 5.5 ton, temperature T = 1,000°C and retention time τ = 60 min*

№	P [ton]	d [mm]	H[mm]	V [cm^3]	G [g]	ρ [g/cm^3]
1	5.5	13.50	27.55	3.82	30.40	7.96
2	5.5	13.50	29.77	4.26	33.99	7.98
3	5.5	13.50	26.42	3.78	30.16	7.98
4	5.5	13.90	25.23	3.58	28.53	7.97
5	5.5	14.00	23.92	3.68	29.26	7.95
6	5.5	13.80	26.02	3.89	31.08	7.99
7	5.5	13.90	25.52	3.87	30.96	8.00
8	5.5	13.70	24.98	3.68	29.48	8.01
9	5.5	13.90	25.98	3.94	31.48	7.99
10	5.5	13.30	28.01	3.89	31.12	8.00

The prototypes were made using a cutting machine, a conventional lathe, a semi-automatic lathe CNC 500SAN-Lynx/220 LM, and a programmable automatic 5-axis CNC machining center Hurco VMX - 30U for the milling.

Figure 4. *Photo of the obtained passive elements*

In Table 5 are shown the physico-mechanical parameters of the composite material from which the prototypes were made.

Table 5. Production parameters and physico-mechanical characteristics of a passive element for high energy impact

1	Force P, [kg]	5,500
2	Average density after pressing ρ, [g/cm^3]	5.25 – 6. 57
3	Density after high temperature sintering ρ, [g/cm^3]	7.44 – 7.95
4	Compressive strength, [kg/cm^2]	4,800 – 5,480
5	Microhardness, [MPa]	925 - 517

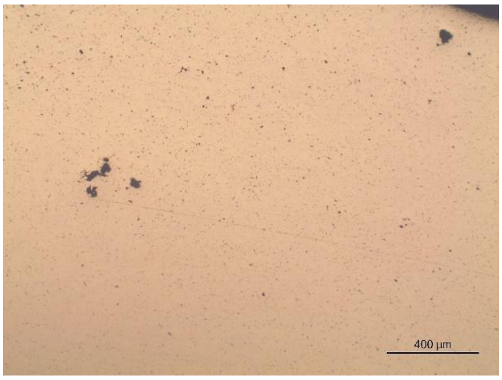
It should be noted that the table shows the average microhardness obtained at five points for each sample.

3. ANALYSIS OF THE MICROSTRUCTURE OF A SAMPLE OF SINTERED COPPER POWDER

Of interest is the structure of the obtained metal-ceramic composite material – see Figures 5 - 8.

Subjected to metallographic analysis was a sample of sintered Cu powder with the following composition: Cu 99.5%; Ag 0.005%; As 0.0002%; Fe 0.005%; Mn 0.002%; Pb 0.05%; Sb 0.005%; Sn 0.005%. To prepare it for analysis of the microstructure, the specimen underwent the standard procedure - embedding in acrylic resin, grinding using glass-paper of grade up to 2,400, mechanical polishing with diamond paste and etching with a solution of 5 ml $FeCl_3$, 30 ml HCl and 100 ml H_2O.

The metallographic analysis was performed using a Reichert-Jung Polyvar Met optical microscope coupled to a ProgRes CT3 digital camera using ProgRes CapturePro image processing software.



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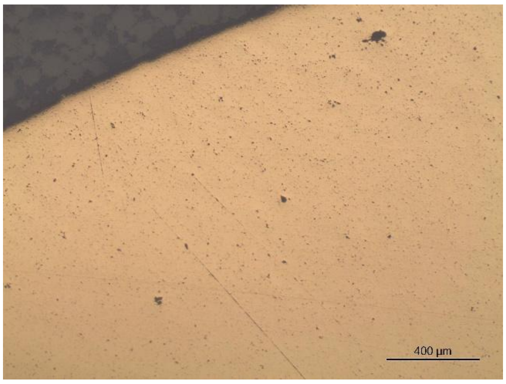

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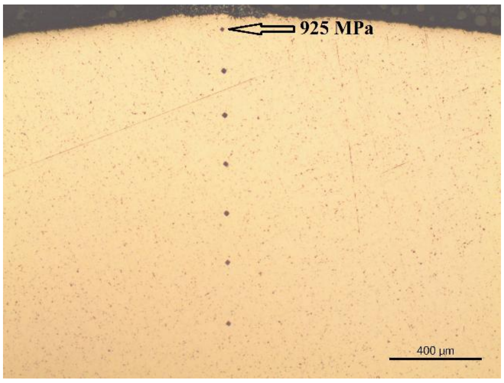
Figure 5. *Microstructure of a polished metallographic specimen*

The microhardness was measured using a MicroDuromat 4000 microhardness meter with a load of 20 gf, a loading time of 10 s and a retention time of 10 s.

Figure 5 shows the microstructure of a polished metallographic specimen. Imperfections in the microstructure are observed in the form of small air cell segments, most of which are located at the periphery of the specimen.

The measured microhardness HV0.02/10/10 of the samples varies from 94.3 kgf/mm^2 (925 MPa) at the periphery of the sample to 52.7 kgf/mm^2 (517 MPa) in its central part. Figure 6 shows the imprints from the measurement of the microhardness at the periphery (Figure 6a) and in the central part (Figure 6b) of the sample.

In a part along the periphery of the specimen (less than ¼ of its circumference), a dark coating layer is observed (Figure 7), with a maximum measured coating thickness of about 93 µm.



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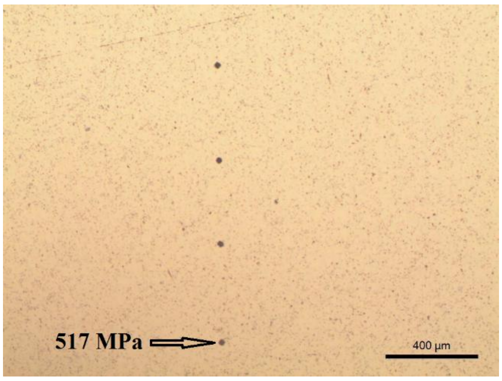

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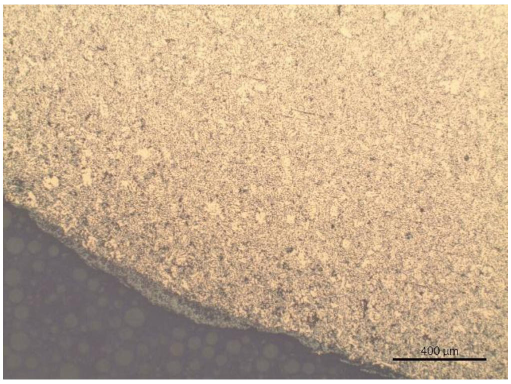
Figure 6. *Microhardness of the specimen along the periphery (a) and its central part (b)*

The measured microhardness of the coating (layer) is 199.5 kgf/mm^2 (1,956 MPa). In machining, this coating layer is removed and the real prototype is obtained only from the inner layer.



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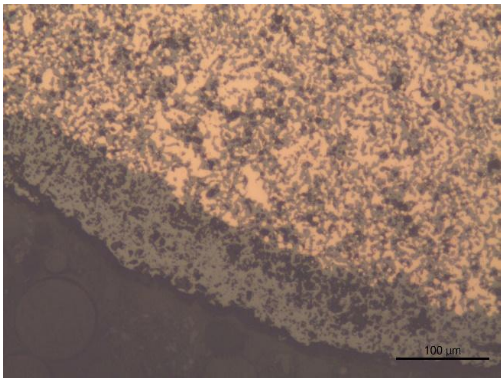

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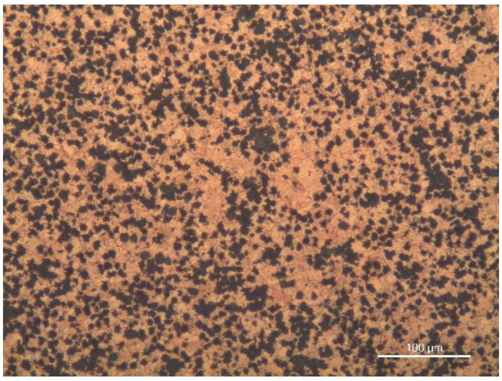
Figure 7*. Coating (layer) in the sample*

Figure 8 shows the microstructure of the sample after etching. A correlation was observed between the measured microhardness in the individual zones and the microstructure. It was observed that it is more pronounced along the periphery (Figure 8b) than in the central part (Figure 8a). Dark areas are observed, which are gray and more densely located along the periphery (Figure 8b) and black in the central part (Figure 8a), where Cu grains with twins can be noticed below the latter.



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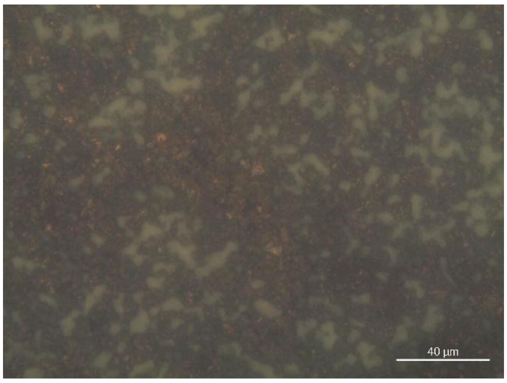

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Figure 8. *Microstructure of the specimen after etching in the central part (a) and at the periphery (b)*

4. CONCLUSIONS

1. The ability to control the density of the obtained non-toxic composite metal ceramics in order to meet the customer's needs, thereby replacing the metal material – in this case toxic lead – is the most important attribute of the obtained material.
2. The ability to formulate and produce this composite material with acceptable physical properties at a sufficiently high relative weight is a challenge that has been overcome.
3. The high density 8 g/cm^3 ±1% composite metal-ceramic material is capable of providing optimum sample weight 4. The new non-toxic, high density composite material is available to engineers and designers for use in applications requiring weight adjustment, balancing, damping, crushing or breaking in sport shooting.
5. The non-toxic material can replace lead and other traditional metallic materials in a more cost-effective way by offering improved physical properties and workability with conventional equipment.

5. REFERENCES

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