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KOMPOZYTY
COMPOSITES

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COMPOSITE SUBSTITUTES FOR LEAD

In the work, research has been taken up on the problem of lead elimination from presently very popular technical applications, through elaboration of its substitutes. It is a problem of utmost importance given the harmful impact of lead on living organisms and the international regulations in force setting out approaching deadlines for total elimination of lead use. Lead has been included in the group of the most toxic substances.

Very promising group of materials in the works on an environmentally-friendly substitute for lead pertains to materials of composite structure. One important component of such a composite is a powder having high density, for instance, made of tungsten or its alloys, or tungsten carbides. The second component is composite matrix, most frequently a polymer. The appropriate material selection of composite components, and particularly the proportion of both the components, enables the attainment the assumed density of composites, varying over a wide range.

The work pertains to elaboration of technology of the materials having a composite structure, containing powder of so called heavy alloy (WHA) having a content of 93%W+5%Ni+2%Fe and polymer or metal matrix. This kind of heavy alloy is traditionally used to manufacture projectile cores. The powder is produced from chips using the impact method. Its price is more than three times lower than that of the tungsten powder, or the original powder of heavy alloy. The basic task was solved in two variants, using as a matrix: Epidian type thermosetting resin and metallic bonding - tin. Two different manufacturing processes of the composites was proposed.

In the first, composite granulate was pressed in the die at pressure of 50÷600 MPa and its polymeric matrix was hardened at temperature of 180°C. In the second process, mixture of WHA and tin powders was pressed in the die at pressure of 600 MPa and next compacts was sintered at 280°C. For each of the variants tests were conducted on the influence of powder content and matrix, as well as of the influence of forming conditions on density of attained composites and their selected mechanical properties.

It has been proven, that there exists a possibility of such selection of material content and of such a manufacturing process, as to attain the densities of composites matching the density of lead - 11.3 Mg/m^3. The results of metallographic tests of attained composites were presented. Additionally and F-Rockwell hardness of the composites were established.

Keywords: **composite, heavy alloy, polymer, powder metallurgy**

KOMPOZYTOWE ZAMIENNIKI OŁOWIU

Podjęto próbę opracowania materiału umożliwiającego wyeliminowanie ołowiu z wielu powszechnych zastosowań - jako jego substytutu. Jest to szczególnie ważny problem, biorąc pod uwagę szkodliwy wpływ ołowiu na żywe organizmy i wprowadzane obecnie międzynarodowe umowy dotyczące całkowitego wyeliminowania ołowiu w najbliższych latach. Ołów został zaliczony do grupy najbardziej toksycznych substancji.

Obiecującą grupą materiałów w badaniach nad opracowaniem przyjaznych środowisku zamienników ołowiu są materiały o strukturze kompozytowej. W takich kompozytach ważnym komponentem jest proszek o dużej gęstości, np. z wolframu lub jego stopu albo węglika wolframu. Drugim komponentem jest osnowa, najczęściej polimerowa. Właściwy dobór materiału obu komponentów, a szczególnie ich proporcji umożliwia uzyskanie wymaganej gęstości kompozytu w szerokim zakresie.

Praca dotyczy opracowania technologii materiałów o budowie kompozytowej, złożonych z proszku tak zwanego stopu ciężkiego (WHA) o składzie: 93%W+5%Ni+2%Fe i polimerowej lub metalowej osnowy. Ten rodzaj stopu ciężkiego jest tradycyjnie używany w produkcji rdzeni pocisków. Proszek tego stopu jest wytwarzany z odpadów i wiórów metodą dynamicznego kruszenia. Jego cena jest trzykrotnie mniejsza niż proszku wolframu albo oryginalnego stopu. Do badań wytypowano dwa rodzaje materiałów osnowy: termoutwardzalną żywicę typu Epidian i proszek cyny. Zaproponowano dwa odmienne procesy wytwarzania kompozytów. W pierwszym prasowano kompozytowy granulat w matrycy przy ciśnieniu 50÷600 MPa, a następnie utwardzano jego osnowę w temperaturze 180°C. W drugim prasowano mieszaninę proszków WHA i cyny przy ciśnieniu 600 MPa, a następnie spiekano w temperaturze 280°C. Określono wpływ zawartości proszku stopu ciężkiego i zawar- tości osnowy, a także wpływ warunków formowania na gęstość uzyskanych kompozytów i wybrane właściwości mechaniczne.

Wykazano, że przez racjonalny dobór składu kompozytów i parametrów procesu wytwarzania możliwe jest uzyskanie gęstości takich materiałów równej gęstości ołowiu, tj. 11,3 Mg/m^3. Przedstawiono strukturę uzyskanych kompozytów i wykazano, że posiadają one jednorodną budowę. Ponadto podano zależność twardości kompozytów od ich składu.

Słowa kluczowe: **krzemionka biogeniczna, spieki, nanoporowatość**

INTRODUCTION

Through the centuries lead found wide application in various fields of human lives. Such applications can be mentioned as examples: water supply tanks and pipes, paints, bearings, coins, and even (in liquid state) as a medieval mean for defending cities. Lead and its alloys were used as printing types, sealing elements or joining components of structures [1, 2]. An unquestioned advantage of lead, from the point of view of its processing, is its relatively low melting point. Lead is also widely used now in mass manufacture of products. These include car batteries, solders in electronics, weights, sinkers, cores of projectiles, etc. Due to its good absorbability of X- and similar rays, lead is widely used in medicine (radiology) and nuclear power generation, as a material for a variety of shields.

Over the last decade, increasing attention has been paid to harmful influence of lead on living organisms, and susceptibility of lead to become accumulated in human bodies. Lead can be introduced into an organism simultaneously with food; it can be inhaled or absorbed through the skin. Lead attacks the central nervous system, kidneys, system of vessels and red blood cells [2, 3]. The removal of lead from the organism is a difficult process.

Lead has been included in the group of most toxic substances. Following this fact, in many research centers around the world intensive research was undertaken to elaborate substitute materials [4-6], and time-limits were assigned for the total elimination of lead from various fields of technology. For instance, year 2006 was the time limit for introduction of leadless solders in the electronic industry.

THE CONCEPT OF A LEAD SUBSTITUTE

It is demanded that the elaborated material should have all advantageous properties of lead and not to have any of its shortcomings. Ideally, the material will:

- have density similar to the density of lead - approx. 11.3 Mg/m^3,
- be non-toxic and unharmful to health,
- be insoluble in the water,
- be easy in processing and forming,
- have better mechanical properties,
- be able to absorb X and gamma radiation,
- have no cancerogenous components,
- have a low price.

The literature analysis has shown that the significant majority of works on an environmentally- friendly substitute for lead pertains to materials of composite structure [6-8]. One important component of such a composite is a powder having high density, for instance, made of tungsten or its alloys, or tungsten carbides. The second component is composite matrix, most frequently a polymer. The appropriate material selection of composite components, and particularly the proportion of both the components, enables the attainment the assumed density of composites, varying over a wide range.

Tungsten as a composite component satisfies the requirements. It has a particularly high density (19.3 Mg/m^3), good mechanical properties even in higher temperature, and the lowest coefficient of thermal expansion among metals. Its fundamental disadvantage is its high price.

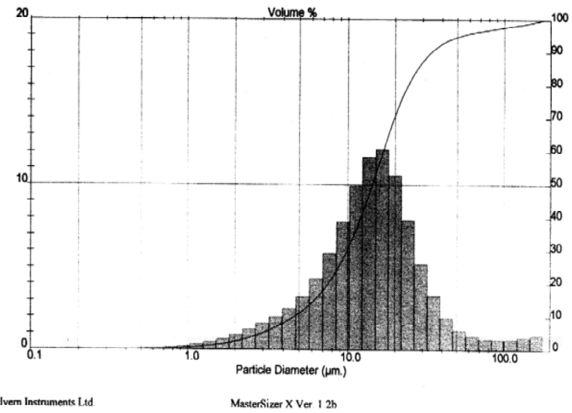

Fig. 1. Analysis of the grain size distribution of the powder

Rys. 1. Rozkład ziarnistości proszku

In this project a so-called heavy alloy (WHA) was applied, having the following composition: 93%W+5%Ni +2%Fe. Material of this kind is used to manufacture projectile cores. Cores are made by turning from rods, so that large quantities of chips are remaining. The powder is produced from chips using the Coldstream impact method. Its price is more than three times lower than that of the tungsten powder, or the original powder of heavy alloy.

The grain size distribution of applied powders shown in Figure 1 is typical for the impact manufacturing method. The predominant fraction forms particles of magnitude 10 to 30 µm, whereas the average size of the particles described by parameter D_{50} is 12.72 µm. Typical shape of grain is presented on Figure 2.

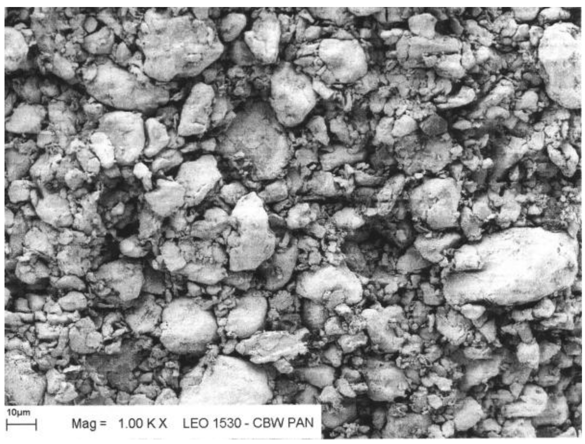

Fig. 2. Typical shape of grain after impact

Rys. 2. Kształt cząstek proszku po rozkruszeniu

It should be noted that theoretical density of the heavy alloy powder is 17.5 Mg/m^3, which significantly exceeds density of lead (11.3 Mg/m^3).

PROPOSALS FOR THE MANUFACTURING PROCESSES

Based on literature and patents publications, as well as on our own experience [9, 10] in forming of composite materials, there were proposed 2 types of the manufacturing processes of material - lead substitute - as follows:

- compacting of composites with thermosetting matrix,
- compacting and sintering of composites with metallic matrix.

For each type of manufacturing process, a concept and method of implementation of subsequent operations was elaborated. Tests of selected physical properties of the compacts, with particular attention paid to their density and mechanical properties were carried out. Based on microstructures, the influence of applied type of manufacturing process on internal uniformity of materials was established.

COMPOSITES WITH THERMOSETTING MATRIX

To manufacture composites with heavy alloy powder, an epoxy resin Epidian 100 was selected. It has the form of a powder, including in its content agents which initiate the process of setting. The setting undergoes in increased temperature.

The proposed method of manufacture of composites is an original work of the project authors [9] and encompasses the following operations:

- weighing of the composite components - the WHA powder and resin in the quantities corresponding to the composite constitution,
- dissolving the resin in acetone,
- mixing of the WHA powder with the resin solution,
- granulating of the moist mass is attained by rubbing through a sieve, of 0.75 mm mesh,
- drying off the granulate,
- weighing of 14 g granulate portions,
- die pressing of granulate portions in ambient temperature, at pressures: 50, 100, 200, 300, 400, 500 and 600 MPa,
- holding at temperature of 180°C over 90 minutes.

Composite compacts had a cylindrical shape, a diameter of 16 mm and were 6÷9 mm high. Their density was established using the geometric method, i.e. the volume was calculated from the measurement of diameter and height (using a micrometer) and the mass of the compacts was weighed with precision balances of 1 mg accuracy. In Figure 3 there are compiled results of the density measurements of three composites containing, by weight: 1%, 2% and 3.66% resin.

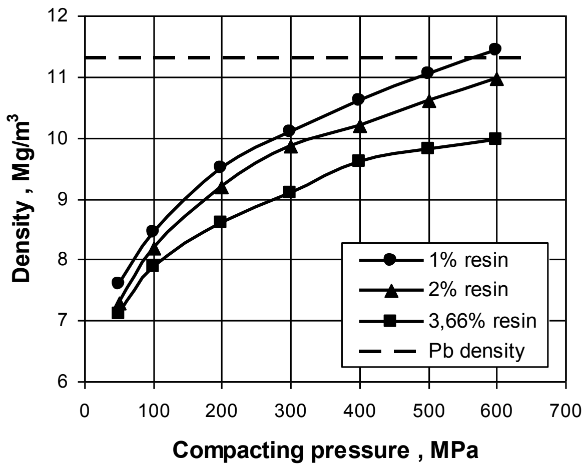

Fig. 3. Density of the compacts containing heavy alloy powder and resin Epidian 100 in 1, 2, 3.66 wt. % after pressing and annealing

Rys. 3. Gęstość wyprasek złożonych z proszku stopu ciężkiego i żywicy Epidian 100 w ilości 1, 2, 3,66% wag. po prasowaniu i wygrzewaniu

From the Figure it can be concluded that the higher the compacting pressure used the higher is the compacts density. Also, the compacts density decreases with the increase of resin content. It is caused by the low density of resin (1.15 Mg/m^3), compared with that of heavy alloy (17.3 Mg/m^3). That is why the relatively low weight content (1÷3.66%) corresponds with the relatively high volume content of resin in composite, as seen in Table 1.

TABLE 1. **Characteristics of composites with matrix of resin Epidian 100**

TABELA 1. **Charakterystyka kompozytów z osnową Epidian 100**

Composite	Resin content by weight %	Volume contents %		Theoretical composite density Mg/m^3
		resin	powder WHA	
I	1	13.4	86.6	15.13
II	2	23.8	76.2	13.45
III	3.66	36.8	63.2	11.35

Composite density close to the density of lead are achieved in compacts with the resin content of 1%, compacted with the pressure of 600 MPa. This value is significantly different from the theoretical density, 15.13 Mg/m^3 (according to Table 1), of such a composite. This follows from the low plasticity of the applied heavy alloy powder, which underwent significant hardening during the production process (impact method).

Figure 4 shows a structure of composite containing 96.34% of heavy alloy powder and 3.66% (by weight) of Epidian resin, compacted at the pressure of 600 MPa.

The composite has uniform structure. WHA particles are spread out uniformly. Particle conglomerates also occur, which is difficult to be avoided, given their small dimensions.

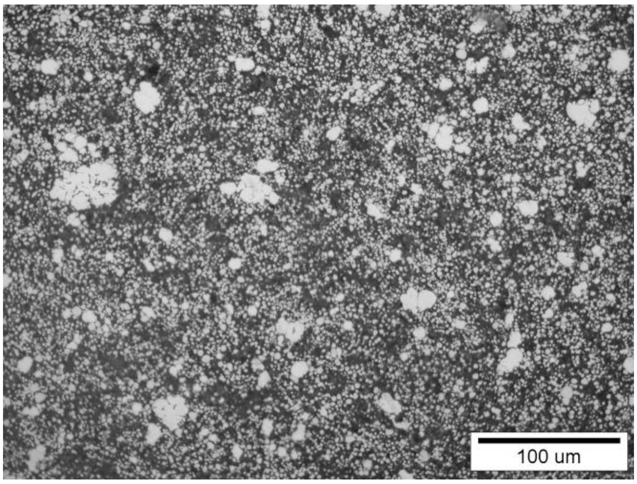

Fig. 4. Microstructure of composite containing 96.34% of heavy alloy powder and 3.66 wt. % of Epidian resin

Rys. 4. Zgład metalograficzny kompozytu zawierającego 96,34% proszku stopu ciężkiego i 3,66% wag. żywicy Epidian

COMPOSITES WITH METALLIC MATRIX

For the metallic matrix of composites with heavy alloy powder (WHA) several metals were proposed: copper, tin, zinc, brass. Tin was selected for tests because of its low melting point (232°C) and ease of conducting the sintering operation with liquid phase. Atomized tin powder marked RSn1 was applied. The average granularity of the powder was approx. 30 μm.

The manufacturing process of the composites consisted of the following operations:

- weighing of composite components,
- mixing of components in a double-cone mixer for 20 minutes,
- preparing mixture samples with specified weight of 10 g,
- pressing of compacts of 16 mm diameter at pressure of 600 MPa,
- sintering of compacts in temperature of 280°C for 40 minutes in protective nitrogen atmosphere.

TABLE 2. **Characteristics of composites WHA/Sn after pressing at p = 600 MPa and sintering**

TABELA 2. **Charakterystyka kompozytów WHA/Sn po prasowaniu przy p = 600 MPa i po spiekaniu**

Content of Sn in composite		Density Mg/m^3		Porosity %
wt. %	% vol.	theoretical	after sintering	
0	0	17.3	11.6	33.2
4	9.0	16.4	11,5	30,0
7	15.1	15.8	11,3	28.5
10	21.0	15.2	11.2	26.0
20	37.2	13.6	10.9	19.9
30	49.6	12.3	10.6	14.1

Table 2 shows the characteristics of manufactured composites, their constitutions, theoretical density, density and porosity after pressing at 600 MPa. The marked composite, having composition of 93% WHA and 7% Sn (by weight), when pressed under the above mentioned conditions attains the desired density, that of lead (Fig. 5). The influence of tin content in composites on their density is shown in Figure 6.

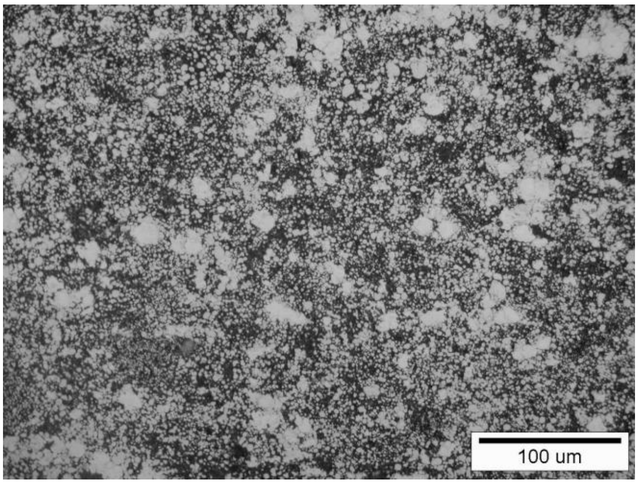

Fig. 5. Microstructure of composite containing 93% WHA powder and 7% Sn after pressing and sintering

Rys. 5. Mikrostruktura kompozytu zawierającego 93% proszku stopu ciężkiego i 7% Sn po prasowaniu i spiekaniu

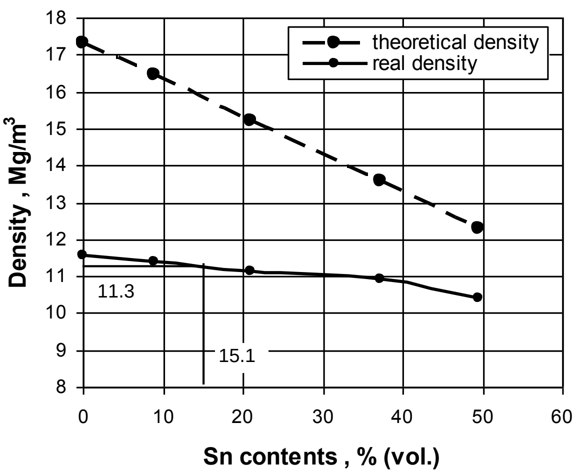

Fig. 6. The influence of tin content (by vol.) on density of composites pressed at p = 600 MPa and sintered

Rys. 6. Wpływ zawartości cyny na gęstość kompozytów prasowanych przy p = 600 MPa i spiekanych

It is characteristic that despite different densities between heavy alloy material (17.3 Mg/m^3) and tin (7.28 Mg/m^3) the density of composites decreases quite gently with the increase of tin content. This is because the curve shape is the result of interaction of two opposing factors: the density increase as a result of introduction of plastic powder and the density decrease caused by the lower density of tin.

Figure 6 also shows the characteristics of changes in theoretical density of composite material, along with increase of Sn content. It is worth noting that for the consecutive composites constitutions the difference between the theoretical density and the real one decreases significantly with the decrease of tin content. As a result, the porosity of the components decreases.

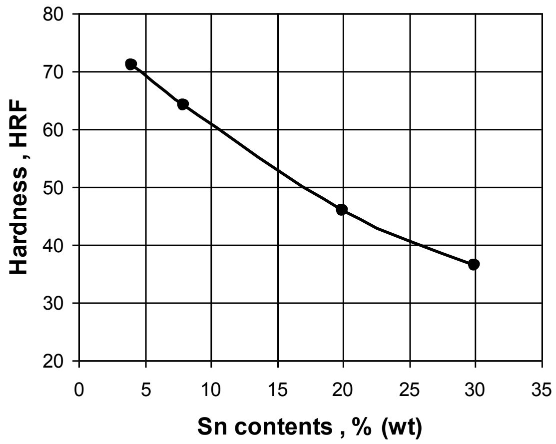

Fig. 7. The influence of tin content on hardness HRF composites

Rys. 7. Wpływ zawartości cyny na twardość HRF kompozytów

The volume of tin in WHA/Sn composites influences their mechanical properties. That is presented in Figure 7. For instance, Rockwell hardness - scale F (load 588 N, ball 1/16”) changes from approx. 70 HRF at Sn weight content of 4% to about 37 HRF at Sn content of 30% [10].

SUMMARY

In the work, research has been taken up on the problem of lead elimination from presently very popular technical applications, through elaboration of its substitutes. It is a problem of utmost importance given the harmful impact of lead on living organisms and the international regulations in force setting out approaching deadlines for total elimination of lead use. In the work, two types of composite materials - thermosetting resin and metallic - were proposed, each varying from one another by the applied matrix. Two processes of manufacturing such composites were proposed. These are original works of the authors, some of them covered by Polish patents. It has been proven that attaining the desired material properties, in particular a density close to the density of lead, is possible.

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