Experimental Researches on Obtaining Sintered Composite Materials with Copper Matrix

R Caliman
“VasileAlecsandri” University of Bacau, Faculty of Engineering, Department of Engineering and Management, Mechatronics, Calea Marasesti 157, Romania

E-mail: rcaliman@ub.ro

Abstract. Conventional and natural materials, limited in quantity or for which high energy consumption is required, are increasingly being replaced by composite materials, as a very good alternative to the exploitation, energy and environmental problems caused by the production of classic. The relative shape and dimensions of the reinforcing component as well as the structure delimit the composite materials reinforced with particles, the filamentary composite materials and the stratified ones. The general properties of the composite materials are decisively influenced by the nature and properties of the constituents, by the volumetric fraction of the reinforcing component and by its orientation in the composite material, as well, as by the mechanical strength of the matrix - fiber/particle interface. The pieces sintered from metallic powders have special physical and chemical characteristics, determined both by the composition and structure of the existing phases, as well as by the size, shape and distribution of the grains. This paper aims to highlight the particularities of the process of obtaining by sintering a category of composite materials with the copper matrix as well as their characterization with regard to the physical-mechanical properties acquired as a result of sintering. Thus, for the production of parts with advanced compactness, the process of double pressing and double sintering is applied. The first pressing is performed with moderate pressures (3000 daN/cm²) and the sintering, at 800°C, with a bearing of about 30 minutes. The second pressing is performed at high pressures (5000 ÷ 6000 daN/cm²) and is followed by the final sintering, under normal regime. Regarding the sintered metal composite materials, with the role of friction, the most important mechanical property is the hardness. This is a function of the bonding forces between the particles, density and degree of resistance of the material at the test site and can be determined by the Brinell method.

1. Introduction

Composite materials are mixtures of associated materials to fulfill a certain characteristic. The obtaining of these materials was dictated by practical considerations because, by combining several components, unique associations of properties can be reached, for example high rigidity and low density. The properties of composite materials can be adjusted for any value, in a wide range, by adjusting their composition. Most of the properties of the composite materials are superior to the properties of the individual components due to the synergy phenomenon [1-4].

Most composites consist of a continuous, majority phase, called a matrix and a minority phase. The minority phase can have three-dimensional geometry (powders, polyhedral particles or round bodies), two-dimensional (lamellae, laminates) or one-dimensional (threads, fibers or filaments). The three-
dimensional materials received the name of dispersed fillings, and the laminates and fibers were named reinforcing agents [5,6].

The powders have an advanced state of separation of the materials, with unconsolidated particles, discrete, of sub-millimetric dimensions, characterized by a large increase of the area of the specific surface, their characteristics are not depending of the type of the obtained method used [7-10].

The powders can be used to obtain advanced, new and special materials such as: composite materials reinforced with particles with metallic or ceramic matrix, friction materials, wear resistant materials, corrosion resistant (stainless) materials, temperature resistant materials high (superalloys), porous materials (filters), ion exchange materials, metallic foams, materials for electrotechnical technologies - heating elements, electrical contacts, electrodes for electro erosion, magnetic materials (soft and hard), materials for tools (molds, cutting tools, grinding tools, reinforced composite materials for tools, etc.), heavy alloys, amorphous materials, nanocrystalline materials, nuclear materials, intermetallic compounds [11-14].

Knowledge metal powder properties are a particular importance for understanding the processes occurring in powder metallurgy. Regarding to the characterization of powders, it is necessary to evaluate the properties of the individual particles (size, shape, chemical composition, microstructure, density, micro-hardness), their common properties and their specific properties, because they generate the characteristics and the behavior of the products in operation. obtained by powder metallurgy [15].

2. Current technologies for obtaining sintered composite materials with metallic matrix
Powder metallurgy can be applied in two situations, namely:
- In order to obtain achievable products and other processes;
- To make products impossible to obtain by other processes.

Pieces made of sintered composite materials through powder metallurgy have a number of technical and economic advantages, including [16]:
- Very high coefficient of use of the raw material;
- High precision products, corresponding to Class H9 and even H7;
- The possibility of replacing expensive or deficient materials;
- High productivity;
- Universal base machine.

The metal powders are obtained by the methods shown in figure 1 [16].

![Figure 1. The general classification of the methods for obtaining the products from metallic powders.](image-url)
2.1. Raw materials
The raw materials for the sintered composite materials are divided into: metal powders; non-metal powders and lubricants and additives.

Studies in the field of powder metallurgy have shown that the properties and quality of sintered products and their manufacturing technology depend largely on the method of manufacturing the metallic powders used as raw material, respectively, on the chemical, physical and technological properties of these powders.

Thus, it can change significantly pressability powder mixture and the porosity formed by pressing and the conditions of diffusion intergranular the degree of homogeneity of the structure of the alloys and pseudoalloys which is formed during the sintering and shrinkage of sintering, namely, the porosity of the final mechanical properties, physical and technology of sintered materials [17-20].

2.2. Sintering of metal powder parts
The technological process for the manufacture of the sintered products is fundamentally different from the technology of classical metallurgy, where the semi-finished products obtained by casting metals and molten alloys are processed by lamination, forging, molding, cutting, etc., thus reaching parts made through a large number of demanding, costly and long-lasting operations. By powder metallurgy, the parts are usually obtained, without the materials and alloys passing through the molten phase. The technological process of manufacturing sintered parts can include the following phases:

- obtaining the raw materials in the form of powders of iron, copper, tin, lead, graphite, lubricants and binders;
- homogenizing the powder or a mixture of powders with the desired composition;
- obtaining by pressing or other methods the tablets from metal powders;
- pre-sintering and sintering of the tablets at high temperatures, in a protective atmosphere;
- calibration of sintered parts;
- mechanical processing or other finishing processing of sintered parts;
- impregnation with oils or easily fusible alloys of sintered parts;
- control and reception of sintered products.

Powder metallurgy ensures sintered products and materials with a precise and uniform composition, with a high degree of properties. Thus, it becomes possible to replace expensive or deficient materials with cheaper and easy to obtain materials, and by this technology, metallic materials and products are obtained that cannot be elaborated by the classical processes, such as: tungsten, pseudo alloys tungsten-copper and tungsten-silver copper [21-23].

2.3. Sintering of alloys in the copper-iron-graphite system

2.3.1. Sintering of copper. Sintering of pure copper occurs in the solid phase, when changing the shape of the pores and reducing their volume determines the decrease of the total surface energy. The specific reduction in volume of the pores, during the sintering of some metallic powders, is calculated with the equations (1) and (2):

\[
V_s = \rho_p \left( \rho_M - \rho_s \right)
\]  (1)

\[
V_p = \rho_s \left( \rho_M - \rho_p \right)
\]  (2)

in which:

- \(V_s\) - the absolute volume of the pores, after sintering;
- \(V_p\) - the absolute volume of the pores, before sintering;
- \(\rho_p\) - tablet density before sintering;
\( \rho_s \) - tablet density after sintering; 
\( \rho_m \) - density of metal.

Figure 2 shows the variation of the \( V_s/V_p \) ratio depending on the density of the tablet before sintering, at different sintering temperatures, for the copper powder.

The value increase of the \( V_s/V_p \) ratio with the increase in tablet density is due to the processes that produce the expansion of the sintered copper materials such as, for example, the expansion of the gas contained in the closed pores.

In the case of copper, diffusion processes are generally responsible for sintering and densification. Volume diffusion is the predominant mechanism.

When sintering copper, we encounter all three stages of sintering in the solid phase, namely:
- the appearance of bonds between particles;
- densification due to recrystallization and disappearance of boundaries between granules;
- Spheroidization of isolated pores.

2.3.2. Sintering in Cu-Fe and Cu-Fe-graphite systems

Sintering of compositions in the Cu-Fe and Cu-Fe-graphite systems is an example of liquid phase sintering due to the relatively low melting temperature of copper (1083°C).

The solubility of Cu in Fe increases with temperature, up to approx. 8.5% Cu, which corresponds even to the sintering temperature of the system (850 °C to 920°C).

Under the conditions of a normal sintering regime, perfect homogenization is not achieved, the properties and the constituent nature of the parts sintered by Cu-Fe deviating from the equilibrium diagram. Usually, the copper powder is added to the iron powder, in order to increase the mechanical strength of the sintered parts.

During the sintering of Cu-Fe tablets, there are dimensional variations that are influenced by the amount of copper in the composition. The expansion of the sintered parts from Cu-Fe is also influenced by a number of technological parameters, including: the size of the copper particles; the duration of sintering and the sintering temperature.

The addition of graphite to Cu-Fe mixtures reduces the dilation of parts during sintering.

The sintering of the parts of the Cu-Fe-graphite system is performed in sintering atmospheres that do not produce decarburization. The sintering temperature must be higher than 1083°C, unless double sintering is used; the first sintering should be done at a lower temperature (850°C).

Choosing an optimal content of Cu (3%) and graphite (1%) allows the production of products whose dimensions do not change by sintering.
A high content of copper powder (7 ÷ 8%) can also have the effect of curbing the diffusion of Cu in Fe and, therefore, avoiding the appearance of secondary cementite in the structure.

3. Experiments on the obtaining and characterization of metal sintered metallic materials with copper matrix

3.1. Elaboration of recipes
Recipes chosen for sintered materials with copper matrix are shown in table 1.

| Table 1. Recipes of metallic materials sintered with the copper matrix. |
|---------------------------------------------------------------|
| Chemical composition (% gravimetric)                      |
| Type of material  Cu  Fe  Sn  Graphite  SiO₂  SiC |
| Cu-1             66.4  10  7.4  3.5    9.7    3  |
| Cu-2             60   10  -   25     -3     4  |

3.2. Preparing the raw materials
The preparation of the raw materials has the effect of removing the impurities and moisture, factors that have a negative influence on all subsequent operations of the technological flow, with repercussions on the properties of the sintered material.

Simultaneously with the removal of impurities, the granulometric dosing is carried out by the powdering operation applied to the powders. Water removal is achieved by keeping hygroscopic powders in the oven at about 180°C.

The raw materials and granulometric fractions used in the prepared recipes were as follows:
- Iron powder < 0.2 mm;
- Copper powder < 0.2 mm;
- Tin powder < 0.2 mm;
- Graphite powder, grade II, dry grade 3, 0.1÷0.3 mm;
- Powder as black SiC, Turda type < 0.12 mm;
- Quartz sand powder, Miorcani type, 0.12 mm.

3.3. Homogenisation of mixtures
The powders prepared according to the preceding paragraph were dosed according to the formulations in table 1 and the resulting mixtures were homogenized in order to achieve homogeneous mixtures, which ultimately ensure good reproducibility of the physico-mechanical properties of the sintered material.

For homogenization, cylindrical laboratory oscillators with inclined axis were used, the homogenization time being 3 hours.

3.4. Sample formation
For the formation of samples from the Cu-1 and Cu-2 mixtures, a cylindrical die having a surface area of 2 cm² was used. Compressed pressures ranged from 5000÷6000 daN/cm². The values obtained for "raw" density are shown in table 2.

| Table 2. The values for "raw" density for copper-based sintered metallic materials. |
|---------------------------------------------------------------|
| No.  Type of material  Compressed pressure (daN/cm²)  Compressed density (g/cm³) |
| 1    Cu-1                5000                      5.41  |
| 2    Cu-1                6000                      5.503 |
| 3    Cu-2                5000                      6.604 |
| 4    Cu-2                6000                      4.67  |
3.5. Sample sintering
The sintering of Cu-1 and Cu-2 samples was carried out in the SAFED tunnel furnace with exo-type protection under the following conditions: sintering temperature: 850°-920°C; gas flow rate “exo”: 4 Nm³/h; furnace speed: 0.6 m/h.

3.6. Testing of sintered samples
A. Density. For sintered samples, density was determined by weighing on the METTLER analytical balance and measuring, with a micrometer, the volume calculation. The values obtained for the density of the metal sintered metal with the copper matrix are shown in table 3.

B. Hardness. The hardness of the sintered samples was determined using the WOLPERT dyemeter, using the following test regime: penetration diameter: 2.5 mm; test force: 62.5 daN; duration of the test: 2 min. The values obtained are shown in table 3.

| No. | Type of material | Compressed pressure (daN/cm²) | Sintered density (g/cm³) | Sintering temperature (°C) | Sintered hardness (HB) |
|-----|------------------|-----------------------------|--------------------------|---------------------------|-----------------------|
| 1   | Cu-1             | 5000                        | 4.94                     | 850                       | 33.8                  |
| 2   | Cu-1             | 6000                        | 5.01                     | 850                       | 32.9                  |
| 3   | Cu-2             | 5000                        | 4.47                     | 850                       | 28.9                  |
| 4   | Cu-2             | 6000                        | 4.64                     | 850                       | 31.9                  |
| 5   | Cu-1             | 5000                        | 4.84                     | 920                       | 29.5                  |
| 6   | Cu-1             | 6000                        | 4.97                     | 920                       | 27.1                  |
| 7   | Cu-2             | 5000                        | 4.52                     | 920                       | 30.6                  |
| 8   | Cu-2             | 6000                        | 4.57                     | 920                       | 31.6                  |

4. Conclusions
The experiments we performed showed the influence of the technological parameters and composition of the materials on the physico-mechanical and tribological characteristics obtained.

In the compositions with the copper base (matrix), we were looking to achieve great results, using fewer constituents in the recipe, so that the technological process is as simple as possible. At the same time, regarding this category of materials, we studied the influence of friction additions such as SiO₂ and SiC.

In experimental research, in addition to the determination of physico-mechanical quantities such as sinter density and Brinell hardness, we also performed an electron microscopy study on sintered compositions. Therefore, we highlighted the basic metal matrix and the distribution of the other constituents.

5. References
[1] Shao G. a.o. 2019 Mechanical properties of graphene nanoplates reinforced copper matrix composites prepared by electrostatic self-assembly and spark plasma sintering Materials Science and Engineering 739 329-334
[2] German R M 2004 Powder Metallurgy no. 8
[3] Zang G-H a.o. 2019 Microstructures and mechanical properties of alumina whisker reinforced copper matrix composites prepared by hot-pressing and hot isostatic pressing Materials Research Express 6(11) 116513
[4] Dash K, Ray BC, Chaira D 2012 Synthesis and characterization of copper–alumina metal matrix composite by conventional and spark plasma sintering Journal of Alloys and Compounds 5165 78-84
[5] Liu Q, a.o. 2019 Effects of morphological characteristics of graphite fillers on the thermal conductivity of the graphite/copper composites fabricated by vacuum hot pressing sintering Vacuum 167 199-206
[6] Shao G a.o. 2020 Effects of graphene nanoplates on arc erosion resistance and wear behavior under electric current of copper matrix composites Journal of Alloys and Compounds 82915 154356.
[7] Wang Hu a.o. 2017 Novel synthesizing and characterization of copper matrix composites reinforced with carbon nanotubes Materials Science and Engineering 6961 80-89.
[8] Ayyappadas C a.o. 2017 An investigation on the effect of sintering mode on various properties of copper-graphene metal matrix composite Advanced Powder Technology 28 7 1760-1768
[9] Hutchings M I 1994 Materials Science and Technology 10 513 – 517.
[10] Nautiyal H a.o. 2019 Copper matrix composites reinforced by rGO-MoS2 hybrid: Strengthening effect to enhancement of tribological properties Composites Part B: Engineering 173 106931
[11] Berdal A and Hoier R 1991 Proceedings of the 12th International Symposium on Material Science in Metal Matrix Composites: Processing, Microstructures & Properties, Ed. Hasen N., Riso Nat. Lab. Hoskilde, Denmark.
[12] Nayan N a.o. 2017 Processing and characterization of spark plasma sintered copper/carbon nanotube composites Materials Science and Engineering - A 682 229-237
[13] Han Bae Y, a.o. 2018 Synergistic effects of segregated network by polymethylmethacrylate beads and sintering of copper nanoparticles on thermal and electrical properties of epoxy composites Composites Science and Technology 1558 144-150
[14] Stefanik P, Sebo P. 1993 Jornal of Materials Science Letters 12 1083 – 1085.
[15] Chawla K K 2005 High-Performance Fiber Reinforcements in Composites, Journal of Minerals, Metals & Materials 47
[16] Davim JP, Marques N, Baptista AM 2001 Effect of carbon fibre reinforcement in the frictional behaviour in a water lubricated environment Wear Elsevier Science 251 1100-1104
[17] *** 2002 Carbone Lorraine Matériaux carbone-carbone, Prospect freins
[18] *** 2002 Carbone Lorraine Freinage a haute energie-Les composites carbon-carbon. Prospect
[19] *** 2002 NASCO Aircraft Brake Inc. - Original Equipment Brake and Wheel Systems, INFO
[20] *** 2002 Carbone Lorraine Airospatiale. AEROLOR Carbon - carbon composites developed by the Gie, INFO Product Line
[21] *** 2002 Carbone Lorraine Airospatiale. Carbon-carbon composites and CERAMETAL sintered metal, Prospect
[22] *** 2002 Carbone Lorraine - Materiaux frittes - materiaux de friction. Prospect
[23] *** 2004 The Automotive Application of Discontinuously Reinforced TiB-Ti Composites (Overview), T. Saito 33-36