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EXPERIMENTAL DETERMINATION OF THE KUCZYNSKI EQUATION FOR THE CASE OF CuSn12 ALLOY SINTERING

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ABSTRACT

Sintered copper-tin alloys are used to obtain products with numerous applications. Some bronze parts such as filters or bushings for self-lubricating bearings can only be produced by specific powder metallurgy technologies. Metal filters represent an important fraction in the field of sintered products. In the paper, measurements of the intergranular bridges were made on the samples obtained by sintering the spheroidal powder from the CuSn12 alloy. Free casting in graphite moulds followed by sintering was used (9 experiments, 3 temperatures x 3 durations). With these data, the coefficients from the Kuczinski equation were determined. Thus, the correlation between the desired porosity for a filter-type product (expressed by the size of the intergranular bridge) and the sintering technological parameters can be established.

KEYWORDS: Kuczynski equation, CuSn12 powder, sintering intergranular bridge, bronze powder filter

1. Introduction

Metal filters are made of sintered materials with porosity over 30%, with communicating pores used in installations that use fluids. The materials, shapes and sizes of these filter components are very diverse and adapted to applications in numerous fields.

There are the following types of materials used for the production of metal filters: *spherical powders, irregular powders, fabrics and fibres*.

For most metal filters obtained by sintering, spherical powders of: *bronze, brass, nickel, stainless steel, titanium, silver, etc. are generally used*.

1.1. Forming procedures of bronze filter elements

The formation of filter elements obtained from powders can be done: without pressing or by pressing. Press forming processes include: *die pressing, rolling, extrusion, injection moulding, etc*. It should be noted that in order to obtain products with sufficient strength, without using high compaction pressures, additional materials must be used (paraffin, polymers, etc.). Otherwise, by applying high compression pressures, which ensure the mechanical resistance necessary for transport and handling to the sintering furnace, too small porosities can be reached, which disqualifies the product from the category of filters. Non-press forming refers to the processes: *free powder casting, free spreading and smoothing, slip casting, spray deposition, vibration forming, etc*. Each process has several technological variants of application of powder formation.

1.2. The pouring freely in the mould

The powder is poured freely into a mould (form) and then subjected to heating for sintering together with it, (Figure 2.1). It represents the simplest method of forming parts from powders, without compression. The homogenization of the powder distribution in the mould cavity is done by vibrating the mould.

The materials from which the forms are made are relatively expensive (refractory alloys, ceramic materials, graphite, etc.), which is a disadvantage, in addition to a relatively short life cycle (considering the repeated thermal cycles to which they are subjected) [2]. The forms made of metal alloys must be subjected to superficial treatments which form layers of stable chemical compounds at the sintering conditions (temperature and protective atmosphere in the furnace). Thus, welding of the form with the sintered product contained therein is avoided [1].

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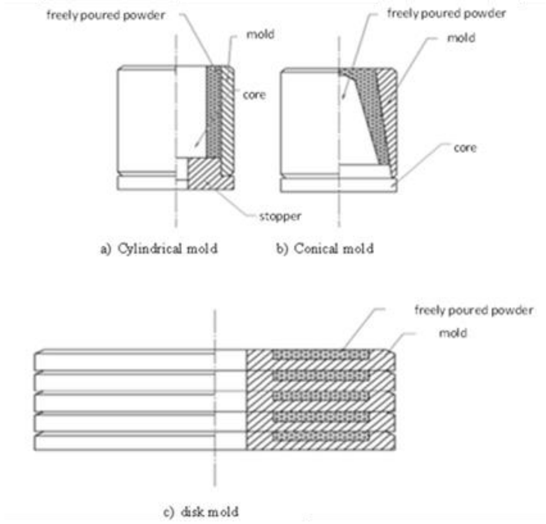

Fig. 1.1. *Powder freely poured into moulds and sintered*

In this work, free casting in graphite moulds was chosen for obtaining the samples, because it is the simplest method, but also because during sintering, graphite provides the protective environment corresponding to the used CuSn12 alloy.

1.3. Kuczinski's equation

The sintering process is governed by the following mechanisms of material transport: diffusion (surface, at grain boundaries, in volume), viscous flow, evaporation-condensation, which develops the formation of sintering bridges (Figure 1.2) [1].

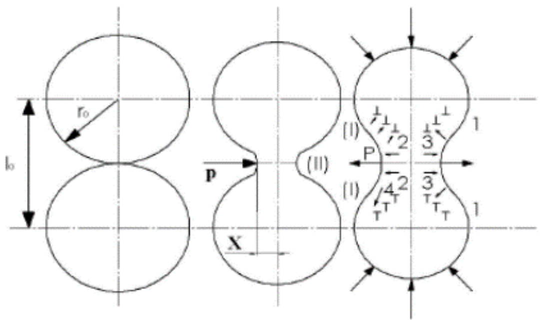

Fig. 1.2. *Principle diagram of the formation of intergranular bridges during sintering*

The studies of the sintering process on regular geometric models of the ball-ball type, led to the establishment of the general form of the law of growth of sintering bridges [1]:

$$\frac{x^n}{r^m} = K(t) \cdot \tau \qquad (1.1)$$

where:

x - half-thickness of the sintering bridge;
r - radius of the powder particle;
τ - sintering time;
K(t) - coefficient depending on the sintering temperature *t*;
m, n - constants dependent on the type of material transfer mechanism during sintering.

The constants m and n are presented in the literature, with relatively concordant values, according to various sources, depending on the mechanism of the predominant material transport [2].

1.4. Manufacture of bronze filters

The sintering of bronze filters formed by free pouring is widely used to obtain filter elements with high permeability. The bronze powders used have dimensions between 0.2÷0.8 mm, with a spheroidal shape. Forming vibration is usually applied for controlled compaction.

For powders with spherical particles of the same diameter, a porosity of 26% can be reached, for a theoretically perfect arrangement. In practice, friction between the particles prevents this level of maximum compaction from being reached, and a porosity of 60 or even 70% can be achieved. By using spherical powders with a certain particle size distribution and controlled vibrations, porosity can be reduced to 35-45%.

In industrial practice, bronze filters are sintered at temperatures above 800 ºC, with a maintenance of 20÷60 minutes, in a protective environment.

2. Experimental research on the sintering of CuSn12 alloy powder

2.1. Objectives of experimental research

The purpose of the experiments was to establish the correlation that exists between the parameters of the sintering thermal treatment (sintering temperature, *t* [°C] and holding time at the sintering temperature, *τ* [min]) and the size of the intergranular sintering bridges, *x* [μm] in the case of products with high porosity, such as filters formed by free pouring from CuSn12 powder. We started from the hypothesis of a correlation like the Kuczinski equation, aiming to find the particular form of this expression for the chosen powder.

2.2. Experimental procedure

The samples were formed in a graphite mould. In this way, the conditions of protection during sintering (reducing environment), the simplicity of

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processing the form, but also the avoidance of welding of the powder to it, were ensured. The mould was made up of two semi-cylindrical components. In one of the parts, a parallelepiped cavity with the dimensions: 38 x 4 x 1.5 mm was processed. (Figure 2.1).

Fig. 2.1. *The mould with the two semi-cylindrical components used for the free casting of CuSn12 powder samples*

After pouring the powder into the mould cavity, a slight vibration was made by applying very light blows to the mould and the excess was removed by scraping. The appearance of the powder prepared for sintering, before mounting the "cap" (which closes the mould cavity), can be seen in Figure 2.2.

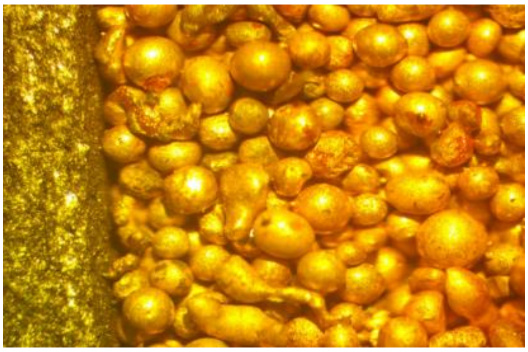

Fig. 2.2. *The graphite mould with the powder prepared for sintering*

In order to preserve as well as possible during sintering, the reducing environment (generated by the presence of graphite), the shape was inserted into an aluminium tube. The ends of the tube were plugged with ceramic felt plugs (Figure 2.3).

Sintering was done in an electric furnace with a LENTON tubular enclosure, with automatic control of the heating regime.

The analysis and measurement of the powder as well as the sintered samples was done with a stereomicroscope (*Carl Zeiss Jena*), equipped with a *TOUPCAM L3CMOS14000KPA* digital camera. The software used for image acquisition and processing was *ToupCam ToupView*.

Fig. 2.3. *The furnace used for sintering and the aluminium tube (to maintain the reducing environment), plugged with ceramic felt plugs, which contains the graphite form*

Statistical analysis of the data obtained by measuring the powder particles under a microscope led to the results in Table 2.1 and Figure 2.4.

Table 2.1. *Granulometric characterization of CuSn12 powder*

Average diameter, d_m[µm]	348
Standard deviation, [µm]	39

Main sintering parameters: sintering temperature, *t*, [°C] and holding time at sintering temperature, *τ*, [min] were used to establish the experimental program according to Table 2.2.

Table 2.2. *Experimental program for CuSn12 powder sintering*

Temperature, ***t***, [°C]	Time, ***τ***, [min]		
800	20	40	60
900	20	40	60
920	20	40	60

The sintered samples (Figure 2.5) were investigated by optical microscopy in order to determine the dimensions of the intergranular bridges: 2x [µm] and the diameters of the particles joined by them: d1, d2 [µm]. The appearance of one of the sintered samples (t = 880 °C, τ = 60 min) analysed by optical microscopy is presented in Figure 2.6. For each of the 9 samples, corresponding to the experienced sintering regimes, 38 sets of measurements were made. A set comprises the size of the bridge between two particles and their diameters.

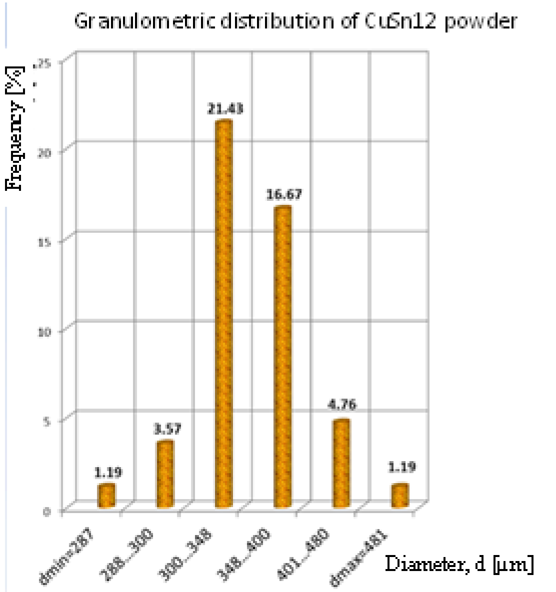

Fig. 2.4. *Granulometric curve of the powder used*

Fig. 2.5. *Appearance of a sintered sample and the mould used for it*

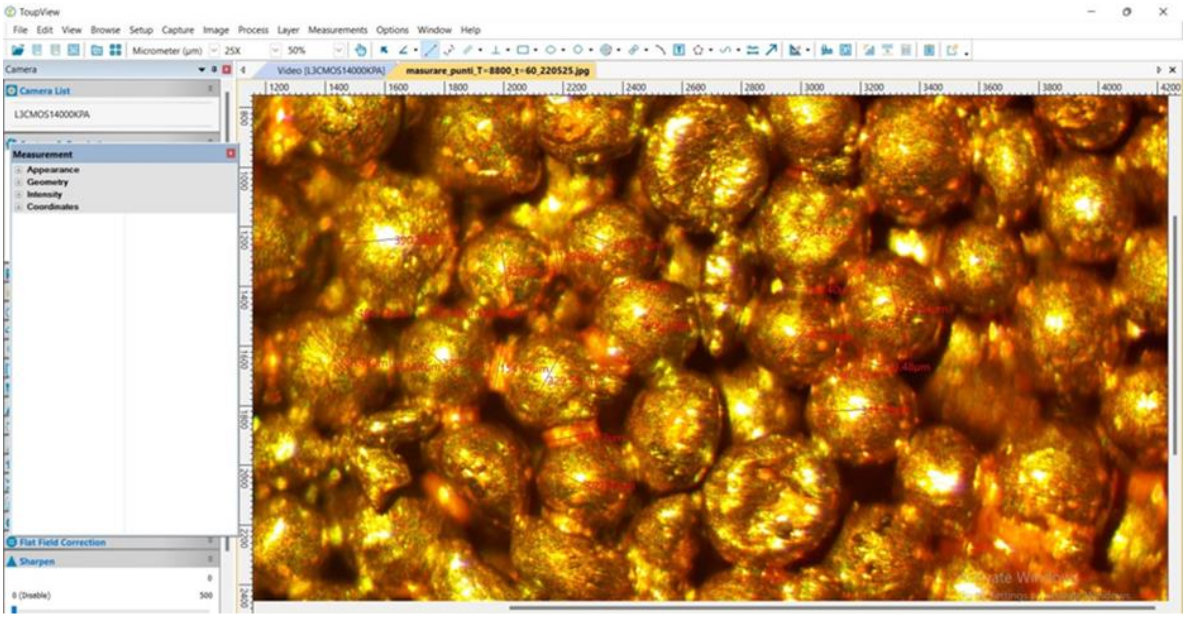

Fig. 2.6. *The appearance of one of the sintered samples (t = 880 °C, τ = 60 min) analyzed by optical microscopy*

2.2. Results obtained

The measurements made on the 9 sintered samples according to the established experimental program (*3 durations x 3 temperatures*) are summarized in Table 3. The r value represents the average of the 76 particles, taken into consideration, in the case of each sample.

With the data obtained, it is possible to identify the particular forms of the Kuczinski equation (1.1) valid for each level of the sintering temperature used:

$$\frac{x^n}{r^m} = K(t) \cdot \tau$$

Table 2.3. *The average sizes of the intergranular bridges and of the particles joined by them*

Sample	Sintering parameters temperature, ***t*** [°C], time **τ** [min]	Average values (38 bridges, 76 particles)	
		x [µm]	***r*** [µm]
1	**t**=880; **τ**=20	61	165
2	**t**=880; **τ**=40	65	164
3	**t**=880; **τ**=60	67	167
4	**t**=900; **τ**=20	72	168
5	**t**=900; **τ**=40	76	165
6	**t**=900; **τ**=60	82	174
7	**t**=920; **τ**=20	82	207
8	**t**=920; **τ**=40	73	164
9	**t**=920; **τ**=60	84	165

Using the data obtained from the measurements made, on the three samples obtained at the temperature of 880 °C, with the maintenance durations of 20, 40, and 60 minutes, it is possible to formulate, starting from the general form of the relationship, a system of three linear equations where the unknowns are *n*, *m* and *K(t)*.

By applying the logarithm function of the Kuczynski expression can be obtained:

$$lg\left(\frac{x^n}{r^m}\right) = lg\,(K(t) \cdot \tau) \qquad (2.2)$$

After processing:

$$nlgx - mlgr - l\,g\,K(t) = l\,g\,\tau \qquad (2.3)$$

For the sintering holding time of 20 minutes the relationship becomes:

$$nlg0{,}061 - mlg0{,}165 - lgK(t) = lg1200 \quad (2.4)$$

If we also use the data obtained for the maintenance times of 40 and 60 minutes, we finally obtain the system of three equations, which contains the sought parameters as unknowns:

$$\begin{aligned} nlg0{,}061 - mlg0{,}165 - lgK(t) &= lg1200 \\ nlg0{,}065 - mlg0{,}164 - lgK(t) &= lg2400 \\ nlg0{,}067 - mlg0{,}167 - lgK(t) &= lg3600 \end{aligned} \quad (2.5)$$

It can be seen that the values for ***r*** and ***x*** have been converted to millimeter and those for **τ** durations to seconds

Solving the system of equations allows identifying the coefficients ***n***, ***m*** and ***K(t)*** so that the Kuczynski equation for samples formed by free casting in graphite molds, from CuSn12 powder sintered at 880°C has the form:

$$\frac{x^{12}}{r^6} = (10^{-12{,}92}) \cdot \tau \qquad (2.6)$$

The other two relationships are obtained following the same procedure. Thus for the temperature of 900 °C:

$$\frac{x^{11{,}14}}{r^{7{,}71}} = (10^{-9{,}84}) \cdot \tau \qquad (2.7)$$

and for 920 °C:

$$\frac{x^{3{,}74}}{r^{4{,}431}} = (10^{-4{,}14}) \cdot \tau \qquad (2.8)$$

The three equations 2.6, 2.7, 2.8 can be written in the form:

$$\begin{cases} \boldsymbol{x = 10}^{\frac{\boldsymbol{lg(\tau)+6lg(r)-12{,}92}}{\boldsymbol{12}}}, for\ \mathbf{t = 880°C} \\ \boldsymbol{x = 10}^{\frac{\boldsymbol{lg(\tau)+7{,}71lg(r)-9{,}84}}{\boldsymbol{11{,}14}}}, for\ \mathbf{t = 900°C} \\ \boldsymbol{x = 10}^{\frac{\boldsymbol{lg(\tau)+4{,}43lg(r)-4{,}14}}{\boldsymbol{3{,}74}}}, for\ \mathbf{t = 920°C} \end{cases} \qquad (2.9)$$

which allows highlighting the more important role of the temperature factor, compared to the one represented by the holding time, regarding the evolution of the size of the intergranular bridges during sintering (***K(t)*** has the maximum value, $10^{-4.14}$, at 920 °C).

3. Conclusions

Based on what is presented in the paper, the following conclusions can be expressed:

1. 9 experiments were programmed, with the parameters of temperature variation and holding time, to identify the coefficients of the Kuczynski relationship, which could describe the evolution of intergranular bridges during the sintering of products formed by free casting, (filter-type products with high porosity) from spherical CuSn12 bronze powder.

2. A set of equations was obtained that describe the evolution, as a function of time, of the intergranular bridge, for a spheroidal powder with a known particle size distribution, sintered at a temperature in the range of 880-920 °C.

3. The Kuczynski equations, customized for the three experimental temperatures, implicitly also include the effects of using a powder with a relatively extensive particle size distribution - the particles of the powder used were spheroidal, with sizes that fall within a relatively wide range, with diameters between 250 and 500 µm.

4. In addition to the dimensional inhomogeneity, the uneven oxidation of the powder particles, which was observed during microscopic analysis, should be noted. The non-homogeneous superficial oxide film in thickness, although it influences the sintering behavior, cannot be taken into account by the Kuczynski equation. That's why the obtained equations should be refined through additional experiments, under the conditions of using a more dimensionally homogeneous spherical powder and with a uniform and as low degree of oxidation.

5. As expected, the obtained equations highlight the much greater influence of the temperature factor, compared to that represented by time, on the evolution of sintering expressed by the variation of the size of the intergranular bridge.

6. It is necessary to establish the quantitative link between the size of the intergranular bridges of the sintered product and its porosity. Thus, it will be possible to correlate the desired porosity with the required sintering regime, based on Kuczynski-type relationships.

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