POROSITY OF SINTERED TIN BRONZES

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The paper aimed at quantifying effects of change of raw materials used for tin bronzes (Cu-Sn mechanically pre-alloyed powders compared to Cu-Sn pure components mixture), and of thermal and temporal sintering parameters on sintered products porosity; the relation between these parameters has been defined mathematically. Compacted specimens made of mentioned raw materials-mechanically alloyed powders and mixture of pure components- have been sintered in several stages; the initiation of the process occurs by pre-sintering in the stability range of α solid solution (360ºC/30'-Transient Liquid Phase Sintering); further thermal processing has been performed in the range of high temperatures, below (SSS) and above the starting temperature of solid solution melting (SLPS), depending on conditions required by experiment programming method chosen. To explicit the relation between sintered products porosity and raw materials as well as sintering parameters has been applied the 2nd order non- linear compositional - orthogonal programming method of experiment. The metallographic evaluation of porosity has been realized with image analysis software. The obtained results under the form of regression relations outline with high probability (95%) the correlations taken into analysis and thus allow the porosity control and evaluation in real processing conditions.

Keywords: tin bronzes, mechanical alloying, sintering, porosity, programmed experiment

1. Introduction

Sintered tin bronzes are used in many applications including self-lubricating bearings and filters which are widely found in practice [1, 2, 3 and 4]. The porous antifriction materials made of tin bronzes are mainly applied for friction couples operating in light conditions – sliding speed lower than 1,5 m/s and applied loads of 0,5÷1,0MPa. The tin bronzes are classified as major materials as it concerns their importance and use [5]. Production of sintered products with specific porosity requires the use of homogenous mixtures of pure components powders, their forming under or without external effort and then sintering at

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temperatures above the melting temperature of minoritary component – tin, in the presence of transient liquids (TLPS).

In these conditions, the melted tin diffuses in the copper matrix and causes pores having sizes and distribution related to the sizes and distribution of tin particles existent before sintering (after forming) [1, 2, 3, 5 and 6]. The increase of sintering temperature up to temperatures below the starting temperature of melting of tin-copper solid solution accelerates the consolidation process kinetics; this develops place according to specific rules of sintering in solid state (SSS) [5]. The development of sintering in these new conditions causes also continuous decrease of porosity level [5, 7 and 8].

The operational properties of sintered components (Cu-10 % Sn bearings bronzes) are strongly influenced by the selection of certain raw materials and processing conditions [4]. Mixtures of pure components powders, copper and tin, are mainly used for production of porous components or of self-lubricating bearings while pre-alloyed powders are applicable to high density components. Unlike the sintering of Cu-Sn powders mixtures, the sintering of pre-alloyed powders lead to densities of about 85-95% of theoretical density of tin bronzes and therefore ensures proper hardness and strength.The compacting behaviour of pre-alloyed powders used for bronze components during sintering in the presence of liquid phase is assessed in [9;12] in order to outline the influence of sintering temperature change and alloying elements of copper on the degree of densification of sintered product.

In the case of strength products requesting significantly lower porosities than those of first category, the forming is to be applied to pre-alloyed powders [1, 2, 3] and thus the initiation of phenomena specific to sintering will occur in matrixes where the minoritary component - tin is extremely fine and uniform distributed on the surface or in the volume of the majoritary component - copper. Therefore, even by sintering in the range of very high temperatures above the starting temperature of melting of solid solution (SLPS) [5], the porosity will be fine and uniform and much lower than that attained in the case of use of powder mixtures and also will decrease rapidly in time. The pre-alloyed powders of tin bronzes possess higher hardnesses than those of pre-mixed powders.

There are quite numerous applications where the products of bronze powders require densities higher than 7,0 g/cm^3. Consequently, the loads necessary for compacting the pre-alloyed powders will be significantly higher than those requested by premixed powders in order to attain the same densities in compacted state (green density) - Fig.1.

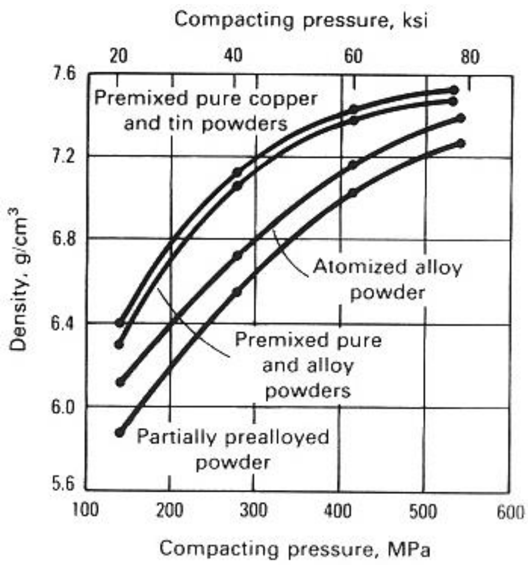


Fig.1 The presability of 90%Cu-10%Sn premixed powders in comparison with that of prealloyed powders [4].

2.Experimental procedure

2.1 Materials used in research

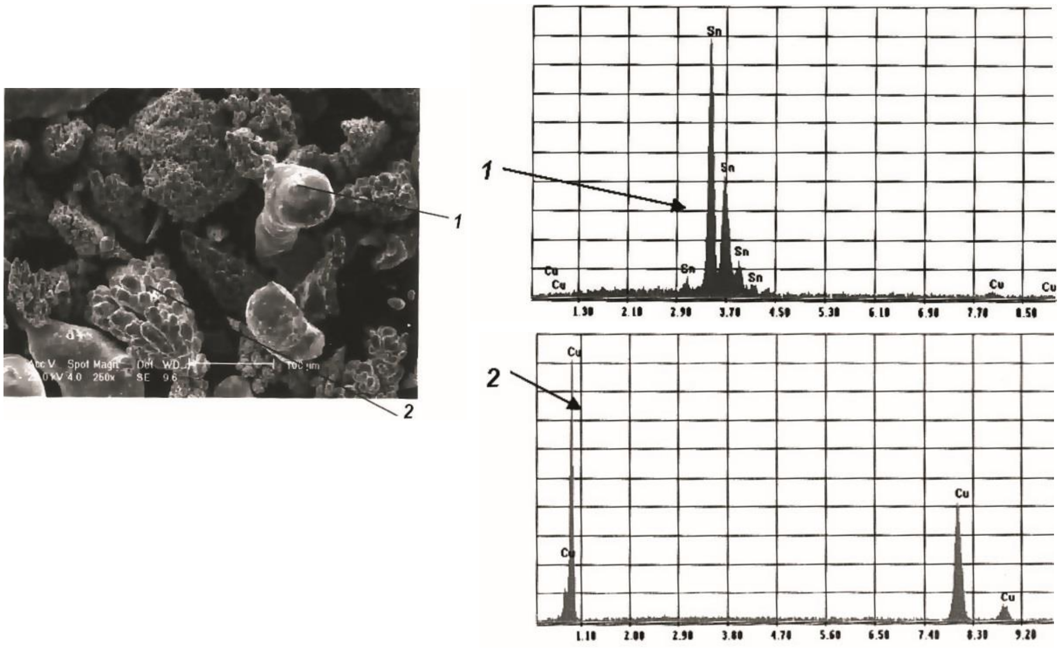
Powders of two metals of interest - copper and tin (the copper obtained by electrolysis and tin by water pulverization) of purity of 99,9% have been used.

The experimental powders fractions had the particle mean diameter in the limits 0.100μm$<d_m<$0.080μm (fraction - 80+100) and apparent densities of 2.5g/cm^3 for copper, respectively 3.7g/cm^3 for tin (determined with Hall funnel).

The powders fluidity (flowrate) taken into analysis and determined by Hall flowmeter has been 28s/50g for copper powder, 16s/50g for tin powder and 27.1s/50g for mixture of 90%Cu-10%Sn+0.75% stearic acid; the acid has been added in order to facilitate mixing and to decrease internal friction between particles during forming operation under pressure.

2.2 Mixing and mechanical alloying

The mixing of required amounts of powders components (90%Cu and 10%Sn as well as 0.75% stearic acid) has been performed for 12 hours in cylindrical mixer with tilted rotation axle; mixer useful space was 1.0 l, mixer frequency was ~ 65 rot/min, tilting angle was 45°. Glass spheres (Φ=10mm) have been introduced inside the mixer in order to amplify the particles movement during rotation of the mixer body and to avoid the segregation and partial pelletization of powders particles. The electronic microscopy investigations (Philips XL30 ESEMtype scanning microscope) - Fig. 2, have outlined the fact that the particles have kept their initial morphology when mixing has been performed in mixers.



Legend. The marks 1 and 2 are corresponding to the particles, respectively to their chemical compositions (a-b).

Fig.2. The morphology and chemical composition of powders particles in mixtures 90%Cu-10%Sn, realized in cylindrical mixers with inclined axle

The mechanical alloying hasbeen realized in mill with balls of WC-Co sintered metallic carbides (Φ = 15 mm÷30 mm) with total weight of 4370 g for 12 hours.The balls milling has taken place by free dropping of balls, mill useful space was 2,5 l and mill effective frequency was 80 rot/min. Mixtures of powders having similar chemical composition with mixtures of premixed powders have been mechanically alloyed.

The electron microscopy (Figs. 3-4) of components processed by balls milling has revealed the different shape of particles - in plaquette (Fig. 3) - in comparison with particles initial shape. The „embedding” of minority component particles -tin in the majority component – copper has been further observed at higher magnifications.

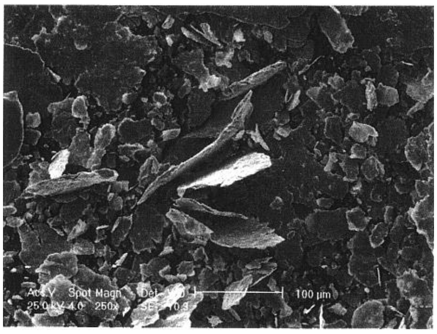
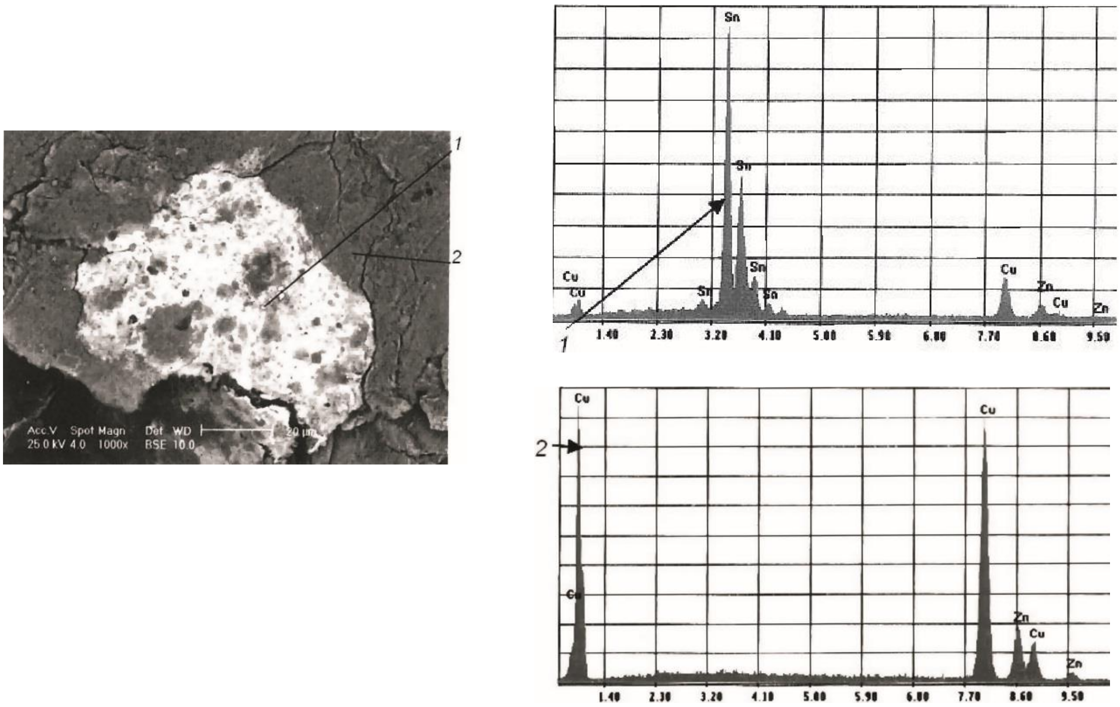


Fig.3 The particles morphology resulted following to the mixing process in balls mills (12 hours, in regime of $n=0{,}80\div0{,}85n_{cr}$)



Legend. The marks 1 and 2 are corresponding to the particles, respectively to their chemical compositions (a-b).

Fig.4 The morphology and chemical composition of powders particles in mixtures 90%Cu-10%Sn, realized by balls milling

2.3 Forming under external effort - Compacting

The compacting has been performed in hydraulic press at compacting efforts up to 600 KN; the die has the internal diameter of 16 mm and the effort is applied unilaterally. The powders mixtures obtained in different conditions have been pressed at the same compacting pressure of 350 MPa independently of previous and subsequent processing conditions. The density of compacted specimens from premixed powders is expected to be higher to that of compacted specimens from partially pre-alloyed powders [10].

2.4 Sintering

The sintering has been performed in neutral medium (nitrogen) in a furnace with automat control of temperature. The pre-sintering has been performed for all processing regimes imposed by the experiment programming method, in identical conditions -360^{o}C/30min, in the presence of transient liquid phase. The sintering in the range of high temperatures, below and respectively above the starting temperature of α solid solution melting, has been realized in accordance with adopted programme (Table 1).

Table1

The matrix of 2nd order non- linear compositional - orthogonal programming (A - mixture 90%Cu-10%Sn obtained in cylindrical mixer with inclined rotation axle; B - 90%Cu-10%Sn mixture obtained in balls mills)

Factor	Z_o	Tempera-ture, ^{o}C, Z_1	Time, min Z_2	Z_1Z_2	Z_1Z_1	Z_2Z_2	Dependent parameters Porosity,P,%	
							$Y_{(A)}$	***$Y_{(B)}$***
Code	X_o	X_1	X_2	X_1X_2	X_1X1	X_2X_2		
Base level, Zo	-	850 (0)	40 (0)	-	-	-	-	-
Variation range, ΔZ_i	-	50	20	-	-	-	-	-
Superior level $Z_0+\Delta Z_i$	-	900 (+1)	60 (+1)	-	-	-	-	-
Inferior level $Z_0-\Delta Z_i$	-	800 (-1)	20 (-1)	-	-	-	-	-
Exp.1	+1	-1/800°C	-1/20'	+1	+1/3	+1/3	**15**	***6***
Exp.2	+1	-1/800°C	+1/60'	-1	+1/3	+1/3	**19**	***9***
Exp.3	+1	+1/900°C	+1/60'	+1	+1/3	+1/3	**3**	***1***
Exp.4	+1	+1/900°C	-1/20'	-1	+1/3	+1/3	**9**	***4***
Exp.5	+1	+1/900°C	0/40'	0	+1/3	-2/3	**4**	***2***
Exp.6	+1	-1/800°C	0/40'	0	+1/3	-2/3	**17**	***8***
Exp.7	+1	0/850°C	+1/60'	0	-2/3	+1/3	**8**	***5***
Exp.8	+1	0/850°C	-1/20'	0	-2/3	+1/3	**12**	***4***
Exp.9	+1	0/850°C	0/40'	0	-2/3	-2/3	**11**	***3***

Legend:

- Xo-fictive variable;

- +1 and -1 is coded parameter values of independently parameters Z_1 and Z2.

The link between the natural and coded values is achieved through correlation:

- Xi = (Zi-Zi0) / ΔZi, where:

- *i is the number experience;*
- *Zi-natural value of independents parameters;*
- *Y_A and Y_B are the natural values of dependents parameters*

Subsequently to soaking at the sintering temperature during the prescribed experimental conditions (Table 1), follows the cooling with the oven in a nitrogen environment up to 300 ° C, then in air. The use of the 2nd order non- linear compositional - orthogonal programming method of experiment to explicit the correlation between the porosity of the sintered tin bronzes obtained is a useful to determine certain solutions - equations in order to anticipate the final porosity. This prediction is valid for both situations taken into analysis (Cu-Sn mechanically pre-alloyed powders compared to Cu-Sn pure components mixture. The porosity of 90%Cu-10%Sn tin bronzes after sintering in different conditions has been metallographically assessed by means of metallographic line composed of Reichert UNIVER microscope, camera for image processing and computer with specialized software for image processing - OMNIMET Enterprise.

3. Results and Discussion

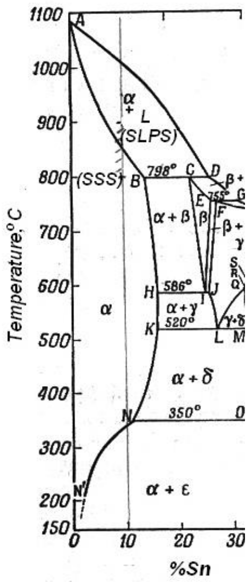
To outline and quantify the implications related to mixtures preparation method and change of sintering parameters in the range of high temperatures, below and respectively above the starting temperature of α solid solution melting (Fig.5), has been chosen the 2nd order non- linear compositional - orthogonal programming method of experiment [11] (matrix in Table 1). The statistical processing of experimental results following to the experiments performed under conditions imposed by the programming method chosen [5] has led to the following particular forms of the interdependencies between sintered products porosity and sintering thermal and temporal parameters such as:

$$Y_{(A)}=P\%=10,88-5,83X_1-1,97X_2-2,5X_1X_2 \quad (1)$$

for sintered compacted specimens of 90%Cu-10%Sn obtained from pure components mixtures by means of mixing in mixers, 12 hours, with tilted rotation axle, and:

$$Y_{(B)}=P\%=4,66-2,66X_1 \quad (2)$$

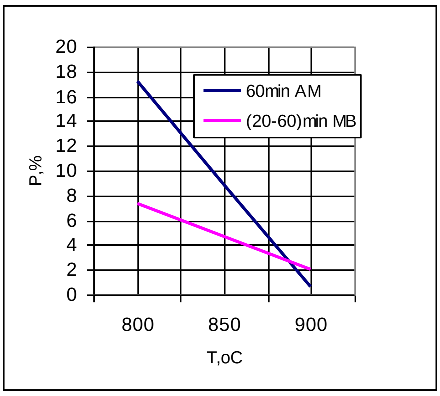
for sintered compacted specimens of 90%Cu-10%Sn obtained from prealloys by means of mixing in balls mills at frequencies at the limits of the steadiness of free dropping regime,12 hours. Note: The equations (1) and (2) are the codified forms of regression equation calculated. The graphical expressions of eq.1 and eq.2 are shown in Fig.6. In the case of eq.1 are taken into analysis the sections through the response surface of the mathematical model corresponding to the different soaking periods at the investigated sintering temperatures in the range [20-60min] (Fig 6b).

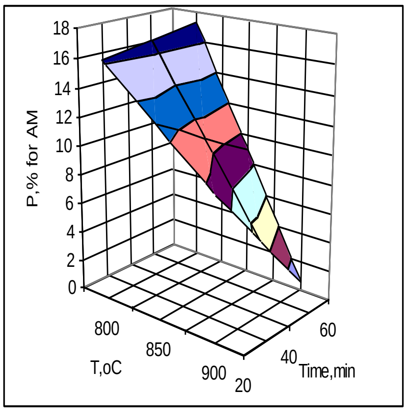


Legend. The temperature range used for experiments is marked in diagram, SSS: Solid-state sintering; SLPS: Supersolidus liquid phase sintering

Fig.5 Cu-Sn Phases diagram (rich copper compositions range)

In the stability range of solid solution (800ºC), by solid state sintering of powders mixtures (90%Cu-10%Sn), the porosity increases slightly with the increase of the soaking period. The increase of difference between porosities of sintered components from premixed powders and of partially pre-alloyed powders by sintering in solid state at 800°C is determined by the initiation of the transient liquid phase (in larger quantities than in the case of premixed powders) in range of low temperatures (360°C/30 min.). The effects in volume of the sintering in different conditions, and implicitly the residual porosity change, are determined by the momentary rapport between pressure caused by atoms fluxes and capillary pressure in the solid phase particles [7]. The porosity increase in the case of sintering in solid state (at 800°C) of pre-mixtures 90%Cu-10%Sn is determined by the continuation of moving by diffusion of tin atoms fluxes in the copper particles volumes in order to homogenize the solid solution (thus, the process previously started in the range of low temperatures is completed during sintering in the presence of transient liquids). The increase of sintering temperature at values close to the (SSS) or higher than solidus temperature (SLPS) related to the solid solution with 10%Sn lead to the porosity decrease due to: 1) pores contraction (their volume diminishes following to the displacement of the particles material in pores and of the embedded gases in counter current to the exterior); 2) pores closing according to a mechanism which is similar to that registered in the case of sintering in solid state of the mono-component systems.





a) b)

Fig.6 Variation of porosity versus sintering parameters: a) Binary diagram P = f (T), for the soaking time constant, b) the ternary diagram P = f (T, t) for sintered specimens made of Cu-Sn mixed powder; ***AM*** *- mixtures in cylindrical mixers with tilted rotation axle;* ***MB*** *- mixtures in balls mills in regime of free dropping.*

Unlike the sintering's developed from pre-mixtures of powders, those made of partially pre-alloyed powders (obtained by mixing in balls mills) are characterized by continuous decrease of porosity during sintering in the range of high temperatures. Similar observations have been found in [3], namely the porosity of components made of Cu-12Sn powders mixtures was higher than that of components made of pre-alloyed powders for sintering in the presence of microwave. In the case of sintering of compacted specimens from partially pre-alloyed mixtures, the porosity is statistically independent on sintering time in the range of 20-60minute. The different behaviour during sintering in the range of high temperatures (in the proximity of solidus temperature related to the α solid solution with 10%Sn) of Cu-10%Sn premixed powders, by comparison with that of partially pre-alloyed powders, is caused by the phenomena developed during sintering in the presence of transient liquids and which led to considerable deviation in the residual porosity level. This way, the homogeneity degree of the solid solution obtained in the sintering stage in the presence of transient liquids of partially pre-alloyed powders is significantly higher than that of sintered premixed powders components. As result, by heating at high temperature the contraction phenomena and further closing of pores are preponderantly observed.

4.Conclusions

By statistical processing of the experimental data obtained by sintering of pure powders mixtures of copper and tin (90%Cu-10%Sn) or of partially pre-alloyed powders, the following conclusions on the residual porosity level have been taken: 1) sintering in the range of low temperatures, in the presence of transient liquids, amplifies the difference between residual porosity of sinterings from premixed powders and that of sinterings from pre-alloyed powders; 2)- sintering at 800°C of mixtures of pure components performed exclusively in solid phase, leads to slight increase of porosity concomitantly with the increase of isothermal soaking period; the increase rate of this characteristic is about 1,59%/h; 3) at higher temperatures, close to the solidus temperature and more intense once with the initiation of the phenomena specific to the supersolidus sintering, the residual porosity is diminishing in time with rates enhanced with temperature increase; 4) in the case of sintering of partially pre-alloyed powders, independently on sintering time (in the range 20-60minute), the porosity is decreasing by about 73%, to variations of temperature in limits 800-900°C; 5) due to the fact that the variation rate of residual porosity during supersolidus sintering of premixed powders mixtures is higher than that registered in the case of partially pre-alloyed powders, after about 50 min on isothermal soaking, the residual porosity of sintered premixed powder components decreases in rapport with that of sintered pre-alloyed powders specimens; 6)- the results expressed under the form of regression equations (eq.1, eq.2) demonstrate with high probability (95%) the correlations taken into analysis and thus ensure the possibility of porosity control respectively of assessment of its level according to specific processing conditions.

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